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Deeper groundwater hazard screening research

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CSIRO Land and Water

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Abbreviations

Abbreviation	Description
APLNG	Australia Pacific Liquefied Natural Gas (project)
СМА	Cumulative Management Authority
CSG	Coal Seam Gas
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DAF	Dilution Attenuation Factor
DNRM	Department of Natural Resources and Mines (Queensland)
EC10	Concentration of a toxicant that causes a 10% lethal effect
EC50	Concentration of a toxicant that cause a 50% lethal effect
HSU	HydroStratigraphic Unit
LC50	Concentration of a toxicant that causes a 50% lethal effect
LoE	Lines of Evidence
LOEC	Lowest concentration of a toxicant tested that causes a significant effect
MATA	Maximum acceptable toxicant concentration
mD	milliDarcy
MODFLOW	MODular groundwater FLOW model
MPA	MegaPAscals
NOEC	No Observable Effect Concentration
NSW	New South Wales
OGIA	Office of Groundwater Impact Assessment (Queensland)
РАН	Polycyclic aromatic hydrocarbons
QGC	Queensland Gas Company
Qld	Queensland
QWC	Queensland Water Commission
US EPA	United States Environmental Protection Agency

Glossary

Term	Description
Aquifer	Rock or sediment in formation, group of formations or part of a formation, which is saturated and sufficiently permeable to transmit quantities of water to wells and springs
Aquitard	A saturated geological unit that is less permeable than an aquifer and incapable of transmitting useful quantities of water. Aquitards often form a confining layer over aquifers
Cleats	Cleats are natural fractures in coal. They usually occur in two sets that are perpendicular to one another and perpendicular to bedding. The cleats in one direction form first and exhibit a high level of continuity. These are called "face cleats". Cleats perpendicular to face cleats are called "butt cleats"
Coal measure	Geological strata of the Carboniferous or Permian periods usually containing coal deposits
Coal seam	Coal seams or coal deposits are layers containing coal (sedimentary rock). Coal seams store both water and gas. Coal seams generally contain more salty groundwater than aquifers that are used for drinking water or agriculture
Coal seam gas	A form of natural gas (generally 95 to 97% pure methane, CH_4) typically extracted from permeable coal seams at depths of 300 to 1000 m Also called coal seam methane (CSM) or coalbed methane (CBM).
Confined aquifer	An aquifer that is isolated from the atmosphere by an impermeable layer. Pressure in confined aquifers is generally greater than atmospheric pressure
Deeper groundwater	Water bearing aquifers, including coal formations, which are generally confined by an impermeable layer (aquitard). They are unconfined where the sediments outcrop. The potential chemical contamination source for deeper groundwater is several hundred meters deep and associated with the coal seam formation targeted for hydraulic fracturing
Depressurisation	The lowering of static groundwater levels through the partial extraction of available groundwater, usually by means of pumping from one or several groundwater bores or gas wells
Dewatering	The lowering of static groundwater levels through complete extraction of all readily available groundwater, usually by means of pumping from one or several groundwater bores or gas wells
Diffusion	The process by which ionic or molecular constituents move under the influence of their kinetic activity in the direction of their concentration gradient
Dispersion or hydrodynamic dispersion	The spread of solutes, colloids, particulate matter, or heat by the combined processes of diffusion and physical mixing of fluids along the path of groundwater flow. This leads to a reduction of concentration at the macroscopic scale
Drawdown	A lowering of the water table of an unconfined aquifer or of the potentiometric surface of a confined aquifer, typically caused by groundwater extraction
Geomechanical	Relating to the movement/expansion/contraction of soil and rock
Groundwater	Water occurring naturally below ground level (whether in an aquifer or other low- permeability material), or water occurring at a place below ground that has been pumped,

Term	Description	
	diverted or released to that place for storage. This does not include water held in underground tanks, pipes or other works	
Groundwater dependent ecosystem	Ecosystems that partially or fully rely on groundwater. These include terrestrial vegetation, wetlands, estuarine and near shore marine systems, river base-flows, cave and aquifer ecosystems and terrestrial fauna	
Groundwater (single phase) flow model	A numerical solution to a partial differential equation used to describe the flow of water in the subsurface. Groundwater flow models involve the flow simulation of a single fluid phase (i.e. water). Common parameters used in groundwater flow models are hydraulic conductivity, specific yield and specific storage	
Hardness	Sum of the ions which can precipitate as 'hard particles' from water. Sum of Ca^{2+} and Mg^{2+} , and sometimes Fe^{2+} .	
Hydraulic conductivity	A coefficient of proportionality describing the rate at which a fluid can move through a permeable medium	
Hydraulic fracturing	Also known as 'fracking', 'fraccing' or 'fracture stimulation', is one process by which hydrocarbon (oil and gas) bearing geological formations are 'stimulated' to enhance the flow of hydrocarbons and other fluids towards the well. In most cases is only undertaken where the permeability of the formation is initially insufficient to support sustained flow of gas. The hydraulic fracturing process involves the injection of fluids, gas, proppant and other additives under high pressure into a geological formation to create a conductive fracture. The fracture extends from the well into the coal reservoir, creating a large surface area through which gas and water are produced and then transported to the well via the conductive propped fracture channel	
Hydraulic gradient	The difference in hydraulic head between different locations within or between hydrostratigraphic units, as indicated by water levels observed in wells constructed in those units	
Hydraulic head	The potential energy contained within groundwater as a result of elevation and pressure. It is indicated by the level to which water will rise within a bore constructed at a particular location and depth. For an unconfined aquifer, it will be largely subject to the elevation of the water table at that location. For a confined aquifer, it is a reflection of the pressure that the groundwater is subject to and will typically manifest in a bore as a water level above the top of the confined aquifer, and in some cases above ground level	
Hydrostratigraphic unit	A formation, part of a formation, or group of formations of significant lateral extent that compose a unit of reasonably distinct (similar) hydrogeologic parameters and responses.	
Imbibition	The process of absorbing a wetting phase into a porous rock. Spontaneous imbibition refers to the process of absorption with no pressure driving the phase into the rock	
Interburden	Material of any nature that lies between two or more bedded ore zones or coal seams.	
Isotherm	A function describing the adsorption/desorption path of solute or gas on solids (e.g. rocks, coal)	
Matrix (rock matrix)	The finer grained mass of rock material in which larger grains/crystals are embedded	
Neumann boundary condition	Also known as a second type boundary condition, involves specification of the derivative that the solution of a differential equation needs to produce along the boundary of a model domain	

Term	Description
Permeability	The measure of the ability of a rock, soil or sediment to yield or transmit a fluid. The magnitude of permeability depends largely on the porosity and the interconnectivity of pores and spaces in the ground.
Porosity	The proportion of the volume of rock consisting of pores, usually expressed as a percentage of the total rock or soil mass
Preferential flow	Preferential flow refers to the uneven and often rapid and short-circuiting movement of water and solutes through porous media characterised by small regions of enhanced flux (such as faults, fractures or other high permeability pathways), which contributes most of the flow, allowing much faster propagation of pressured differences and transport of a range of contaminants through that pathway
Probability density function	A function that describes the relative likelihood for a random variable to take on a given value
Recharge	Groundwater recharge is the process whereby surface water (such as from rainfall runoff or irrigation) percolates through the ground to the water table
Regional-scale groundwater models	Models that encompass an entire groundwater system, geological basin or other significant area of interest that extends well beyond the measurable influence of individual bores or borefields
Reservoir (hydrocarbon)	A subsurface pool of hydrocarbons (i.e. oil and/or gas) contained in porous or fractured rock formations. Naturally-occurring hydrocarbons such as crude oil or natural gas are typically trapped in source or host rocks by overlying low permeability formations
Solute	The substance present in a solution in the smaller amount. For convenience, water is generally considered the solvent even in concentrated solutions with water molecules in the minority
Spatial interpolation	The procedure of estimating the value of properties at unsampled sites within the area covered by existing observations
Stratigraphy	An arrangement of sedimentary, metamorphic and/or igneous rocks
Unconfined aquifer	An aquifer in which there are no confining beds between the zone of saturation and land surface
Unconventional gas	Natural gas found in a very low permeability rock, such as coal seam gas, shale gas, and tight gas. Unconventional gas such as coal seam gas is trapped in coal beds by adsorption of the gas molecules to the internal surfaces of coal. It cannot migrate to a trap and form a conventional gas deposit. This distinguishes it from conventional gas resources, which occur as discrete accumulations in traps formed by folds and other structures in sedimentary layers
Well	Borehole in which a casing (e.g. steel piping) has been placed to restrict connection to specific ground horizons/depths

Symbols

Symbol	Brief description and unit of measurement
С	Predicted environmental concentration (mg/L)
Co	Initial concentration (mg/L)
Cads	Adsorbed (or solid phase) concentration (mg/L)
C _{liq}	Liquid phase concentration (mg/L)
DL	Longitudinal dispersion (m ² /day)
D _{TH} , D _{TV}	Horizontal and vertical transverse dispersion (m ² /day)
Ea	Activation energy (kJ/mol)
E _h	Redox potential (mV)
foc	Fraction of organic carbon (g/g)
foc_r	Fraction of organic carbon, rescaled (g/g)
k	Permeability [m²]
К	Hydraulic conductivity [L.T ⁻¹]
κ	Rate constant (1/day)
K _d	Solid-liquid partition coefficient (L/kg)
K _{eq}	Equilibrium partition coefficient at a given temperature (L/kg)
k _h	Horizontal permeability [m²]
Кос	Organic carbon partition coefficient (L/kg)
K _{OW}	Octanol-water partition coefficient (L/kg)
k _v	Vertical permeability [L ²]
n	Total porosity (-)
λ	First-order transformation or decay constant (day-1)
λ	Longitudinal dispersivity (m)
$\lambda_{TH,\lambda_{TV}}$	Horizontal transverse dispersivity and vertical transverse dispersivity (m)
μ1,μ2	First-order biodegradation constants (day ⁻¹)
$ ho_{ m b}$, $ ho_{ m s}$	Dry bulk density (g/cm ³) and solid density (g/cm ³ of solids)
R	Universal gas constant (8.314 x 10 ⁻³ kJ/K/mol)
R _f	Retardation factor (-)
Т	Absolute temperature (K)
t _{1/2}	Chemical half-life (1/day)
V	Linear fluid flux [m/day]

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Summary

The main purpose of the project 'Deeper groundwater hazard screening research' is to deliver a number of enabling science products that can be used to assess risks that may arise if chemicals used in coal seam gas extraction enter deeper groundwater'. Final products include a "proof-of-concept" tiered hazard screening framework, developed and tested in at least two separate study areas, and associated protocols. The framework is developed considering that the main chemical source is present in deeper groundwater (injected drilling and hydraulic fracturing fluids, and geogenics) and the main chemical transport pathway is via deeper groundwater. This framework will allow a rapid screening to determine which chemicals are more likely to be hazardous when emitted into deeper groundwater environments and may thus present potential risks to the environment and human health. Application of the framework will allow chemicals with low hazard levels to be readily excluded from separate, more detailed assessments of environmental and human health risks associated with deeper groundwater contamination. This further provides a robust evidence base to inform future research priorities into the fate of coal seam gas chemicals. This study is not an assessment of the risk of any actual or proposed coal seam gas extraction project. The chemicals chosen for the study are representative and any concentrations or conditions of use, while based on known practices, are notional.

This project complements the *National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia* (the *Assessment*). The Assessment aimed to develop an improved understanding of the occupational, public health and environmental risks associated with chemicals either used in or mobilised by drilling and hydraulic fracturing for coal seam gas in an Australian context. The Assessment looked at chemicals used in drilling and hydraulic fracturing for coal seam gas within a sample time period to develop a stronger understanding of the chemicals used in the industry and what risks they may pose to coal seam gas workers, the public and the environment. The assessment considered potential risks to human health and the environment associated with surface-related exposure pathways of chemicals used in drilling and hydraulic fracturing for coal seam gas. These include surface water, soils, and shallow unconfined groundwater systems. Unlike the current project, the Assessment did not consider the effects of potential risks to deeper groundwater. Here deeper groundwater refers the water bearing aquifers, including coal formations, which are generally confined by an impermeable layer (aquitard). They are unconfined where the sediments outcrop. The potential chemical contamination source for deeper groundwater is several hundred meters deep and associated with the coal seam formation targeted for hydraulic fracturing.

The deeper groundwater hazard screening methodology described in this report involved development of a two-level hazard screening framework that identifies (at a Level 1) chemicals 'of low concern' and chemicals that require a more detailed Level 2 analysis because they could not be screened out at Level 1. The Level 1 screening used existing lists and rules for screening chemicals and lists of chemicals that have previously been rigorously assessed and found to be of low concern to the environment and/or human health (that is, "chemicals of low concern"). The Level-2 analysis involved integration of:

- conceptual models with plausible fate and transport release pathways and simplified calculation tools for
 estimating the degree of attenuation (expressed as dilution attenuation factor [DAF]) that chemicals would
 experience prior to potentially reaching receptors,
- spatial analyses of proximity (horizontal distance) between potential contaminant sources at CSG wells and
 receptor locations identified in two case study areas (one in the Surat basin [Queensland] and one in the
 Gunnedah basin [New South Wales]) and derivation of proximity-frequency relationships for each group of
 receptors,
- information on attenuation due to chemical or biological degradation, geological processes (sorption onto
 organic and/or mineral phases) and flow-related processes (dilution/dispersion) for a selection of characteristic
 coal seam gas chemicals (hydraulic fracturing and geogenic chemicals), and iv) solute particle tracking analysis to
 identify likely connectivity, travel distance and time between the coal seam formaton being hydraulically
 stimulated and groundwater related receptors.

The current study only applies to intentional chemical releases into deeper groundwater, including coal measures. Importantly, the study's results and techniques should not be applied to surface-related risks, where more established techniques should be employed to assess environment and human health risks.

The major findings of this research are that:

- based on a literature review involving mainly US studies, hydraulic fracturing operations appear not to present a significant environmental risk to deeper groundwater resources and groundwater dependent ecosystems, except when abandoned or suspended well casings are intersected by fracturing fluids during the high-pressure stage of fluid injection. Furthermore, maintaining good well integrity was found to be the key to minimising many of the risks associated with hydraulic fracturing and unconventional resource extraction,
- the likelihood of each of four plausible fate and transport release pathways are either unlikely (with high or very high confidence) or extremely unlikely (<5% probability) in an Australian context,
- the spatial analysis of proximity of ecologic, economic and socio-cultural receptors to CSG wells in subdomains of the Gunnedah and Surat Basins indicated the majority of receptors were at large (km) to very large (tens of km) distances from existing or planned CSG wells,
- particle tracking-based pathways calculated in the subdomains of the Gunnedah and Surat Basins were shown to
 have a relatively small number of potential connections between existing receptors and coal seam gas wells.
 Where connections did exist, the travel time through groundwater was determined to be very long, from
 hundreds to tens of thousands of years,
- particle tracking-based pathway calculations undertaken with an entire well field to capture possible cumulative
 effects from mass accumulating in tens and possibly hundreds of hydraulically fractured wells reveals that, for
 the conditions of the case study area, the likelihood for chemicals released through multiple wells contributing to
 a single receptor are small,
- calculated attenuation potential for organic compounds based on degradation constants (half-lives) obtained from the literature indicated that for the long travel times typical of the two case study areas, chemical/biological degradation processes together with sorption would easily reduce chemical concentrations to 'low concern' level,
- calculated attenuation potential due to dilution and dispersion provided another line of evidence that for the large travel distances a significant decrease in chemical concentration can be expected (for both organic and inorganic chemicals),
- to yield concentrations of coal seam gas chemicals in groundwater that are 'of low concern' to aquatic ecosystems, sufficient attenuation can be obtained after a travel distance of 2 km or less due to the dilution and dispersion processes; higher dilution can be obtained for chemicals subject to degradation and sorption,
- bore integrity, well spacing, and using chemicals with shorter half-lives were found to be key to minimising risks to contamination of deeper groundwater.

In conclusion, the usability of the hazard screening framework has been demonstrated, and dilution attenuation factors (DAFs) derived, for a limited set of chemicals, exhibiting widely differing properties (mobility, persistence, toxicity) that would permit a sufficiently broad understanding of potential risks across the currently used chemicals. Development and "proof-of-concept" testing have been conducted using data in two separate study areas. Hypothesis-driven research has been used to develop quantitative tools for identifying potential hazards to human and environmental health from chemicals associated with coal seam gas extraction (primarily drilling and hydraulic fracturing chemicals). Such tools will also assist with communicating the hazards and risks to regulators, industry, and the community. The tools are uniquely placed to provide insight in the dominant processes and conditions that govern fate, mobility, persistence, and ultimately exposure.

The overall conclusions from this study suggest that the risks arising from contamination of deeper groundwater by hydraulic fracturing chemicals are likely to be very small under conditions such as those found in the two case study areas.

Multiple lines of evidence have been developed to underpin this conclusion. Although a systematic uncertainty analysis was not undertaken and beyond the scope of this project, a simplified sensitivity analysis was instrumental in providing reasonable bounds around output values. A systematic qualification of predictive uncertainty is recommended for future research.

1. Introduction

This project 'Deeper groundwater screening hazard research: National assessment of chemicals associated with coal seam gas extraction in Australian' delivers a "proof-of-concept" tiered, hazard-screening framework for identifying chemicals used in coal seam gas extraction in Australia that may be a potential hazard to human health and aquatic and groundwater dependent terrestrial receptors¹. The project considers potential contamination in deeper groundwater and potential transport pathways via deeper groundwater to water bores and aquatic and terrestrial receptors linked to surface water environments. This framework will allow a rapid screening to determine which chemicals are more likely to be hazardous and which may present potential risks to the environment and human health. The framework will be developed and tested in two separate study areas. Application of the framework will allow chemicals with low hazard levels to be readily excluded from separate, more detailed environmental risk assessments. This also provides a robust evidence base to inform future research priorities.

This project complements the *National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia* (the Assessment) (NICNAS 2017a). The Assessment aimed to develop an improved understanding of the occupational, public health and environmental risks associated with chemicals either used in or mobilised by drilling and hydraulic fracturing for coal seam gas in an Australian context. The Assessment looked at chemicals used in drilling and hydraulic fracturing for coal seam gas within a sample time period to develop a stronger understanding of the chemicals used in the industry and what risks they may pose to coal seam gas workers, the public and the environment. The potential chemical contamination source is at or near the surface, therefore only shallow groundwater was considered in the Assessment. Unlike the current project, the Assessment did not consider the effects of potential risks to deeper groundwater. Here deeper groundwater refers to the water bearing aquifers, including coal formations, which are generally confined by an impermeable layer (aquitard). They are unconfined where the sediments outcrop. The potential chemical contamination source for deeper groundwater is several hundred meters deep and associated with the coal seam gas related chemical source (drilling fluids, hydraulic fracturing fluids, and geogenics) to distant receptors will generally take tens to hundreds of years during which natural attenuation takes place which reduces initial concentrations to negligible levels.

It should be noted that sublethal toxicity effects of contaminants such as endocrine disruption are not considered in this study. Similarly, the effects of mixtures of contaminants are not considered as the ecotoxicological data to develop the required concentration additive models of mixture toxicity are not available.

Contamination of groundwater resources as a result of hydraulic fracturing for gas production requires the presence of a contamination source, a pathway and a driving force. The contamination source relates to the residual fraction of hydraulic fracturing fluid not recovered during the water extraction required for gas production. Indeed, hydraulic fracturing fluids injected into coal seam wells will to a large degree be recovered from coal seam pore waters during normal well operations (Mallants et al. 2017a). A residual fraction may remain in the pore waters of the coal seam formations, especially at the fringe of the fractured zone and within micro-fractures and micro-pores within coal and coal seam formation sediments (Santos 2014). Adsorption of hydraulic fracturing chemicals onto coal and host formation sediments will further contribute to some fraction of the chemicals remaining in the CSG well fields and potentially in adjacent formations, especially if natural connectivity via tectonic windows between these formations exists.

Depending on the ambient flow rate compared to the flow rate induced by CSG extraction, hydraulic fracturing chemicals may migrate away from the well fields towards irrigation, stock or other extraction bores placed within coal seam aquifers. For instance, although the Walloon Coal Measures in the Surat Basin in Queensland, Australia, are considered to be an aquitard at the basin scale, they can form aquifers in particular near the basin margin. In the Surat Basin, groundwater from the Walloon Coal Measures is currently extracted from 1647 groundwater bores for stock, domestic, industrial and

 $^{^{1}}$ The terms receptors and assets are used interchageably

urban purposes (OGIA 2016). In the Bandanna Formation of the Bowen Basin in Queensland, there a further 103 groundwater bores for town water supply, agriculture and industry (OGIA 2016).

Hydraulic fracturing chemicals could potentially also find a pathway into overlying or underlying aquifers through hydraulically active faults and/or hydraulic fracturing-induced preferential flow paths (Davies et al. 2012; Warner et al. 2012a; US EPA 2012a, 2013; Kissinger et al. 2013; Reagan et al. 2015; DoEE 2017a). Additional pathways might exist through water bores exhibiting poor integrity and exploration bores that provide inter-aquifer connectivity (Jackson et al. 2013; Wu et al. 2016).

Some of the key research questions regarding potential deep groundwater contamination that are addressed in the current research include:

- What is the long-term adsorption, and thus attenuation potential of coal for hydraulic fracturing-related chemicals?
- Once the key attenuation reactions in the deeper groundwater have been accounted for, what are the contaminant concentrations along the chemical pathways, and what chemicals warrant further assessment and fate-pathway analysis?
- Are there any pathways in deep groundwater that provide a connection between the contaminant source and receptors such as (deep and shallow) water bores?
- Based on coupling groundwater flow with the coal seam contaminant source, what is the minimum travel time to potential receptors, and what is the chemical concentration and toxicity in the receiving groundwater connected surface waters?
- What are the timescales within which significant microbiological and/or chemical transformation/degradation of hydraulic fracturing-related contaminants could occur?
- Does such degradation result in metabolism products that are sufficiently mobile, of significant concentration, or sufficiently toxic that they warrant further assessment?

Hypothesis driven research could be used to quantify potential risks to human and environmental health from drilling, cementing, and hydraulic fracturing chemicals, and could be used to develop tools to assist with communicating the risk to regulators, industry, and the community. Geochemical modelling approaches, when combined with laboratory-based solute and ecotoxicological investigations, could help answer the above research questions.

These questions have been addressed by undertaking research in the following areas:

- identifying the exposure pathways (i.e. likelihood and consequence of connectivity) between groundwater contamination sources and key receptors in the receiving environment that should be included in risk assessment processes;
- quantifying the potential for hydraulic fracturing chemicals to mobilise otherwise immobile geogenic contaminants in the coal seam, and assessing the potential human and environmental health risks arising from exposures to these geogenic contaminants via groundwater transport processes;
- determining the thresholds of test bed species to selected hydraulic fracturing chemicals, and of Australian aquatic flora and fauna more generally;
- including the effects of potential well integrity failures and misdirected hydraulic fracturing in a risk assessment
 process aimed at (i) evaluating enhanced transport of contaminants into aquifers adjacent to the coal seam(s), and (ii)
 predicting the extent of downstream groundwater dilution if such emissions occur;
- developing an efficient methodology for predicting environmental concentrations at specified sites post fracturing, such that the risk to human health and environmental receptors can be assessed at these locations;
- developing a decision-making framework that can assist decision makers and industry to determine the risks to human health and the environment.

1.1. **Recent risk assessments and current knowledge gaps**

The National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia (the National CSG Chemicals Assessment project) carried out an assessment of potential risks to human health and the environment associated with surface-related exposure pathways of chemicals used in drilling and hydraulic fracturing². These include surface water, soils, and shallow unconfined groundwater systems. Consistent with previous US EPA assessments (US EPA 2004a, 2010, 2011), the National CSG Chemicals Assessment project did not examine the risks posed by chemicals to deeper groundwater systems such as confined aquifers³.

At present, the interactions between deeper subsurface systems and processes, hydraulic fracturing processes, the long-term fate of anthropogenic and geogenic chemicals, and potential human and environmental risks from drilling, cementing, and hydraulic fracturing chemicals are all poorly understood.

As a result, our ability to predict the risk of deeper groundwater contamination from hydraulic fracturing is limited. Furthermore, there is a paucity of knowledge to assess if contamination of shallow groundwater and connected surface waters would also present a possible risk through natural or enhanced connectivity between deeper and shallow groundwater.

Several recent studies, including an OWS Background Review on Hydraulic Fracturing (Commonwealth of Australia 2014a), the National CSG Chemicals Assessment (Apte 2017a, 2017b, Jeffrey 2017a, 2017b), an OWS workshop, and reviews by the NSW Chief Scientist and Engineer (2014a, 2014b, 2014c, 2014d), have all documented knowledge gaps that prevent a robust quantification of risks to deeper groundwater. According to these reports, current knowledge gaps include:

- details of the drilling, cementing, and hydraulic fracturing chemicals used (such as concentrations, physico-chemical and ecotoxicological data); improved analytical methods for quantifying chemicals in flowback and produced water
- the fraction, identity and concentration of fracturing chemicals that are recovered in flowback and produced water, and the persistence of those chemicals and their metabolites in the coal seam water, which is often under high pressure and temperature
- mobilisation and fate of geogenic contaminants and to what degree interactions with hydraulic fracturing fluids can enhance their mobility
- prediction and design of safe hydraulic fracture stimulation producing fractures that do not risk growth into an aquifer; leading practice guidelines for fracture growth modelling
- short- and long-term well integrity and the risk of additional pathways providing connectivity between coal seam formations and beneficial aquifers
- toxicological data against which to assess environmental exposure risk, and
- numerical modelling capabilities including reactive attenuation of chemicals, possibly via fracture-like pathways.

Based on the expert reviews summarised above, additional outcome-driven research into deeper groundwater risk would better define the potential for hydraulic fracturing to mobilise naturally occurring geogenic chemicals, and inform our understanding of the risk that anthropogenic and geogenic chemicals might pose for selected receptors. An improved evidence base could be used to more directly inform regulators' perceptions of risk, whilst industry would be better informed and better able to manage any associated risks.

² <u>http://www.nicnas.gov.au/communications/issues/fracking-hydraulic-fracturing-coal-seam-gas-extraction</u>.

³ http://www.nicnas.gov.au/communications/issues/fracking-hydraulic-fracturing-coal-seam-gas-extraction/information-sheet.

1.2. Methodology

The tiered hazard screening framework used in this study involves a two-level analysis: Level 1 involves a high-throughput screening of chemicals that have previously been rigorously assessed and found to be of low concern to the environment and/or human health (that is, "chemicals of low concern"), while at Level 2 chemicals not screened out at Level 1 are further assessed to allow ranking of the relative chemical hazard on the basis of a calculated dilution attenuation factor (DAF) (Figure 1-1).

Level 1 screening involves consideration of data on health effects and ecotoxicity and the intrinsic physico-chemical properties of the chemical that will affect potential exposure. The Level-1 screening is site-independent, as it does not include exposure assessments. The Level-2 analysis combines:

- spatial analyses of contaminant source-receptor, distance-frequency relationships,
- chemical, biological and geological attenuation information for characteristic chemicals,
- the conceptual models, application protocols and calculation tools required to estimate the degree of attenuation that chemicals would experience prior to potentially reaching receptors.

The Level-2 analysis involves development of conceptual models and associated calculation tools for hazard screening based on the possible fate pathways and geochemical and physicochemical property data as metrics to estimate the likelihood that the chemical could reach and impact on receptors such as drinking water resources. The conceptual models take into account the local hydrogeology of basins, based on best available hydrogeological information. Chemical fate and transport is influenced by environmental and site-specific conditions, therefore additional information for a hazard screening may include the likelihood for a fluid pathway to develop between the coal seams being subject to hydraulic fracturing as a potential pathway for contamination.

The final hazard screening tools developed as part of this research project have both site-independent (Level-1 screening) and site-dependent (Level-2 assessment) components. These hazard screening tools include the following research products (see Figure 1-1):

- Reseach Product 1. This hazard screening tool can be used to identify:
 - i) chemicals of low concern to human health and the environment that do not need further assessments, and
 - ii) chemicals that cannot be classified as 'of low concern' and therefore require further assessments.
- Research Product 2. The chemical transport pathway analysis tool is site-dependent, but a broad set of flow conditions are covered giving the final analysis a high level of applicability.
- Research Product 3. The spatial analysis is site-dependent, but will again cover a wider range of proximity data which will allows making some general inferences about likelihood of exposure.
- Research product 4. This includes a compilation of attenuation parameters that are in part site-independent (for example, *K*_{oc} and half-life), and in part site-dependent (for example, *K*_d, using rock-specific sorption data or using organic carbon content).
- Research product 5. The dilution attenuation factors DAF developed as part of this research have a sitespecific basis, although the approach taken will give it a broad degree of applicability.

When selecting the test case areas as part of the Level-2 assessments, care has been taken to have a sufficiently broad coverage of hydrogeological conditions and features that would give the analysis a sufficient level of generality, rather than being too site-specific. Nevertheless, this analysis cannot describe all possible conditions of groundwater flow and attenuation relevant to all Australian CSG basins. The nuts and bolts of the hazard screening framework will be illustrated on the basis of the case studies, without claiming to provide a nation-wide coverage. The analysis undertaken with the screening framework should provide insights to address the questions regarding potential deep groundwater

contamination and potential transport pathways via deeper groundwater to aquatic and terrestrial receptors. After describing the method and applying it in two basins the report goes on to discuss how to apply these methods in other basins.



Figure 1-1 Workflow of the hazard screening framework.

1.3. **Report Structure**

The present report begins with conceptual models developed to inform the screening of hazards associated with chemicals used in coal seam gas extraction and deeper groundwater (Chapter 2). These conceptual models include plausible fate and transport release pathways and description of biological receptors, chemical screening based on toxicity, and simplified exposure calculations for plausible pathways. In Chapter 3, spatial analyses are undertaken of CSG extraction activities, hydraulic fracturing operations and relevant receptors. These involve determination of contaminant source-receptor, frequency-distance relationships using geographical information systems (GISs) and relevant databases with key receptors. In Chapter 4, information will be collated on chemical persistence (half-life) and mobility (retardation) to improve understanding of attenuation processes in deeper groundwater. Such information is pivotal to estimating potential for attenuation of indicator chemicals at the receptor. The integrated hazard screening framework that combines i) source-receptor distance-frequency relationships, ii) chemical, biological and geological attenuation information, iii) exposure assessment for plausible conceptual models and, iv) toxicity, is discussed in Chapter 5. A summary of outcomes and outputs is provided in Chapter 6.

2. Development of conceptual models to help screen hazards associated with chemicals used in coal seam gas extraction and deeper groundwater

The focus of this chapter is on i) a national and international literature review with a focus on plausible pathways, hazard screening approaches, toxicity, exposure assessments (Section 2.1), ii) chemical screening based on toxicity, simplified exposure calculations for plausible pathways (Section 2.2), iii) selection of chemicals for proof-of-concept-testing (section 2.3), iv) developing conceptual models with plausible fate and transport release pathways (Section 2.6), and v) identification of receptors for use in the spatial analysis (Section 3).

2.1. Literature review

A national and international literature review has been undertaken which covers:

- investigations regarding possible chemical fate and transport pathways that affect potential exposure routes for sensitive receptors (Section 2.1.1). This includes a review of published compliance reporting in Queensland, Canada, and the USA.
- existing approaches for hazard screening applicable to coal seam gas extraction and deeper groundwater (e.g. the Multi Criteria Decision Analysis Framework developed by US EPA (2016a) and substitution regimes implemented in the North Sea) (Section 2.1.2).
- a summary of risk assessment approaches undertaken by industry and regulators (Section 2.1.5).
- a review of toxicity data regarding human health effects and ecotoxicity, and estimation methods to predict toxicity values (see Table 2-1 for an overview of literature sources used) (Section 2.1.5).

Table 2-1. Selection of sources of information used in literature review.

ltem	Subject description	Source
Plausible pathways	Hydraulic fractures: How far can they go?	Davies et al. 2012
	Hydraulic-fracture-height growth	Fisher and Warpinski 2012
	Geochemical evidence for possible migration of Marcellus formation brine to shallow aquifers in Pennsylvania	Warner et al. 2012a
	Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction	Jackson et al. 2013
	Hydraulic fracture height limits and fault interactions in tight oil and gas formations	Flewelling et al. 2013
	Modelling the transport of fracturing fluids, brine and methane	Kissinger et al. 2013
	Fugitive emissions from CSG equipment and well casings	Day et al. 2014
	Seepage pathway assessment for natural gas to shallow groundwater during well stimulation, in production, and after abandonment	Dusseault and Jackson 2014
	The fate of residual treatment water in gas shale	Engelder et al. 2014
	The integrity of oil and gas wells	Jackson 2014
	Coal seam gas water: potential hazards and exposure pathways in Queensland	Navi et al. 2015
	Simulation of the environmental impact of hydraulic fracturing of tight/shale gas reservoirs on near-surface groundwater.	Reagan et al. 2015
	Potential impacts of hydraulic fracturing on drinking water resources.	US EPA 2016a
	Bore and well induced inter-aquifer connectivity: a review of literature on failure mechanisms and conceptualisation of hydrocarbon reservoir-aquifer failure pathways	Wu et al. 2016
	Onshore gas well integrity in Queensland, Australia	GasFields Commission Queensland 2015
	Simulation of loss of fluid from a hydraulic fracture into an aquifer	Jeffrey et al. 2017a

	Literature review for coal seam gas hydraulic fracture growth and well integrity	Jeffrey et al. 2017b
	The geometry of a hydraulic fracture growing along a wellbore annulus	Bunger et al. (2010)
	Evaluating Hydraulic Fracture Effectiveness in a Coal Seam Gas Reservoir from Surface Tiltmeter and Microseismic Monitoring	Johnson et al. (2010)
	Hydraulic fracturing in faulted sedimentary basins: Numerical simulation of potential contamination of shallow aquifers over long time scales	Gassiat et al. (2013)
	Deep groundwater contamination risk from hydraulic fracturing considering current industry practice	This report, Appendix 7
Exposure assessments	Assessment of safe setback distances for the public in case of explosions, radiant heat, toxic gas clouds, and air pollution from hydraulic fracturing	Haley et al. 2016
	Environmental risk assessment involving issues identification, hazard and exposure assessment, and risk characterisation	QGC 2012
	Qualitative hazard assessment and quantitative risk assessment of hydraulic fracturing fluids	Santos 2014
	Synthesis of available scientific literature and data to assess the potential for hydraulic fracturing for oil and gas to change the quality or quantity of drinking water resources	US EPA 2016a
	Hydraulic fracturing in unconventional gas reservoirs: Risks in the geological system	Kissinger et al. (2013)
	Coal seam gas water: potential hazards and exposure pathways in Queensland	Navi et al. (2015)
	Numerical simulation of the environmental impact of hydraulic fracturing of tight/shale gas reservoirs on near-surface groundwater: Background, base cases, shallow reservoirs, short-term gas, and water transport	Reagan et al. (2015)
Hazard screening approaches	As above	US EPA (2016a)
	Environmental risk assessment process with emphasis on hazard analysis and risk assessment for chemicals proposed for use in petroleum andand geothermal activities	DMP 2013
	Criteria for classifying substances hazardous to health	Commonwealth of Australia 2004
	Identification of chemicals of low concern to human health, Inventory Multi-tiered Assessment and Prioritisation Framework	NICNAS (2015)
	Development of the partition coefficient (Kd) test method for use in environmental risk assessments	Adey (2005)

Chemical and biological attenuation	Sorption of trace constituents from aqueous solutions onto secondary minerals	Ames et al. (1983)
	Comprehensive study of organic contaminant adsorption by clays: Methodologies, mechanisms, and environmental implications	Boyd et al. (2011)
	Some aspects of the properties and degradation of polyacrylamides	Caulfield et al. (2002)
	Toxicity profile of labile preservative bronopol in water: The role of more persistent and toxic transformation products	Cui et al. (2011)
	Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces	Haderlein et al. (1993)
	Biocides in Hydraulic Fracturing Fluids: A Critical Review of Their Usage, Mobility, Degradation, and Toxicity	Kahrilas et al. (2014)
	Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments	Piatt et al. (1996)
	Sorption of trace elements on natural particles in oxic environments	Tessier (1992)
	Understanding variation in partition coefficient, Kd values. Volume II: Review of geochemistry and available Kd Values for cadmium, caesium, chromium, lead, plutonium, radon, strontium, thorium, tritium (3H), and uranium	US EPA (1999a)
	In situ spectroscopic investigation of adsorption mechanisms of nitroaromatic compounds at clay minerals	Weissmahr et al. (1997)
Toxicity data and estimation methods	ECOSAR: Estimating toxicity of industrial chemicals to aquatic organisms using the ECOSAR (ECOlogical Structure-Activity Relationship) class program	US EPA 2012b
	Toxicological Profile for 2-butoxyethanol, 2-butoxyethanol acetate, Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, arsenic, barium, cresols, HMX	ATSDR (1997, 1998, 2005, 2007a, 2007b, 2008)
	Approved Criteria for Classifying Hazardous Substances	Commonwealth of Australia (2004)
2.1.1. Plausible pathways

2.1.1.1. Summary of review findings from international studies

Hydraulic fracturing for coal seam gas production has a 40-year history, with more than 20 years of commercial experience in North America prior to the recent development of the Australian CSG industry. There has been a commensurate development of modelling approaches and relevant experimental and field data to understand and predict hydraulic fracture growth. In CSG hydraulic fracturing design, one of the most important considerations for the effectiveness of the treatment is preventing unwanted vertical hydraulic fracture growth out of the CSG production interval into the overburden geological layer. Such height growth is ineffective and inefficient from a production viewpoint and therefore the topic has received much attention.

This topic is also pertinent from a groundwater contamination viewpoint as vertical hydraulic fracture growth is often highlighted as a potential contaminant transport pathway to water bearing aquifers.

This review of national and international studies concentrates on estimating the vertical extent of a hydraulic fracture and any other plausible pathways that may be stimulated or reactivated during a CSG hydraulic fracturing treatment.

Contamination of groundwater resources as a result of hydraulic fracturing for gas production requires the presence of a pathway and a driving force. For contaminant migration to occur, a natural or induced pathway is required. This could include:

- pathways created during hydraulic fracturing,
- fracturing processes that connect the reservoir to pre-existing pathways (e.g. faults),
- pathways created during well drilling and casing operations (Wu et al. 2016),
- drilling and casing operations providing connections to pre-existing pathways (Reagan et al. 2015).

In addition to a pathway such as fractures and faults, a driving force is required for flow and transport of hydraulic fracturing fluids and reservoir fluids, and gas. Subsurface processes that may drive flow and transport include propagation of injected pressurised fluids, natural hydraulic gradients in case of overpressurised reservoirs, or depressurisation causing release of natural gas.

The question whether pathways can be created or whether pre-existing pathways are transmissive has been addressed in the literature in broadly two ways: i) conceptual studies based on monitoring data (e.g. micro-seismicity during fracturing) and ii) simulation studies. The latter typically involves identifying the parametric space under which fluid release may occur. Most of the published studies are from US shale gas areas where horizontal drilling is combined with creating vertical fractures (Brantley et al. 2014). Because in Australian CSG coal formations vertical drilling is the rule (certainly in Queensland, some horizontal wells have been drilled in the Gunnedah basin in NSW - Rutovitz et al. 2011; NSW Chief Scientist and Engineer 2014b), with fracturing operations aimed at producing mainly horizontal fractures, extrapolation of results from the US shale-based studies to Australian CSG gas fields is the much greater depth of the hydrocarbon resource in the US.

The possibility for pathway formation due to hydraulic fracturing has been well studied (e.g. Flewelling et al. 2013; Fisher and Warpinski 2012; Davies et al. 2012; Jackson et al. 2013). These studies have all been undertaken for tight gas conditions in sedimentary basins in the US. Such sedimentary basins are typically dominated by low-permeability rocks such as shale, siltstone, and mudstone. As a result, upward fluid movement will be minimal in the absence of conductive fractures or faults. Furthermore, the low degree of water saturation in shale formations causes any introduced water to be tightly bound by capillary forces. In these restrictive environments, the potential for upward fluid migration will depend primarily on the extent of upward fracture growth and fault movement (Flewelling et al. 2013). Flewelling et al. (2013) evaluated the physical limits on hydraulic fracture growth or fault movement and how such limits might factor into an analysis of potential fluid migration to shallow aquifers. They analysed over 12,000 hydraulic fracturing stimulations whose fracture networks were mapped with micro-seismic sensors. A simple physical relationship was derived that describes the upper limit on fracture height growth as a function of hydraulic fracturing fluid volume. The analysis assumed that naturally occurring joints and faults are sealed and that upward fluid migration can only occur along these features when they are opened or induced to slip. They concluded that:

- maximum fracture heights and the overall vertical extent of seismic displacements during hydraulic fracturing stimulations are ultimately limited by hydraulic fracturing fluid volume
- it is not physically plausible for induced fractures to create a hydraulic connection between deep black shale and other tight formations to overlying potable aquifers, based on the limited amount of height growth at depth and the rotation of the least principal stress to the vertical direction at shallow depths.

Using real data collected from micro-seismic and micro-deformation mapping on thousands of hydraulic fracturing jobs carried out in the most active shale plays in the US, Fisher and Warpinski (2012) concluded that hydraulic fracture heights are relatively well contained owing to a number of containment mechanisms. Based on an analysis of mineback experiments involving real hydraulic fractures, containment mechanisms were found to include complex geologic layering, changing material properties, formation of hydraulic fracture networks, and natural barriers to propagation owing to higher confining stress or high permeability which allows the fluid to bleed off. As an example, Figure 2-1 presents a hierarchy of fracture complexity. Rather than the simpler planar fracture shown in the upper left, fractures in common geologic environments display varying degrees of complexity. Owing to this complexity, fractures are believed to grow shorter than they would if they were simple planar features.



Figure 2-1 Schematics of levels of hydraulic fracture networks (Fisher and Warpinski 2012).

Davies et al. (2012) undertook a comprehensive compilation of micro-seismic data from hydraulic fracturing events in US shales. They concluded the probability that stimulated hydraulic fractures extend vertically beyond 350 m is approximately 1% (Figure 2-2). They argued there are certain geological scenarios where there could be connectivity between a hydrocarbon reservoirs and aquifers through a significant thickness of overburden. The example discussed by Davies et al. (2012) was when sand proppants are used that can cut through 1000 m of shale (Hurst et al. 2011). When combined with long enough pumping time, this could cause critical pressurisation of shallower strata and therefore shallower fractures. These and other geological scenarios should be considered and modelled.



Figure 2-2 Frequency of hydraulic fracture height for (a) upward and (b) downward propagating fractures in the Marcellus, Barnett, Woodford, Eagle Ford and Niobrara shales. Probability of exceedance of height of (c) upward propagating fractures and (d) downward propagating fractures (Davies et al. 2012).

In a geochemical study of potential connectivity between Marcellus shale and shallow groundwater, Warner et al. (2012a) classified 426 water samples from shallow groundwater in an 80 × 160 km area of northeastern Pennsylvania currently experiencing hydraulic fracturing of the Marcellus gas shale. The classification consisted of 4 groups based on Br, Cl, Na, Ba, Sr, Li concentration and the isotopic ratios of ⁸⁷Sr/⁸⁶Sr, ²H/H, ¹⁸O/¹⁶O, and ²²⁸Ra/²²⁶Ra. Evidence that diluted residual brine had migrated from deep formations along cross formational pathways was found in the chemistry of one group with high Br/Cl and Sr/Ca but low ⁸⁷Sr/⁸⁶Sr. By referring to the source as the "Marcellus", Warner et al. (2012a) implied that leakage was from the Marcellus and they suggested that the pathways of natural gas leakage might be areas of higher risk for leakage of residual hydraulic fracturing fluid (the fluid left in place beyond the control of engineers). The Marcellus was portrayed as leaking now without any human assistance through cross-formational pathways and the concern was raised that hydraulic fracturing in the Marcellus could make this leakage worse. According to Engelder et al. (2014) the possibilities raised by Warner et al. (2012a) are extremely unlikely (see further). In a reply to earlier criticism of Engelder (2012), Warner et al. (2012b) argued that (i) there is evidence for natural migration of brine and subsequent dilution in shallow drinking water aquifers, and (ii) if hydraulic fracturing intercepts natural pathways (i.e., faults/fractures) that connect the Marcellus to overlying units, the migration of fluids, including gases, remains possible.

Jackson et al. (2013) analysed 141 drinking water bores across the Appalachian Plateaus (northeastern Pennsylvania, US) examining natural gas concentrations and their isotopic signatures with proximity to natural gas wells. Analytes included methane (CH₄), ethane (C₂H₆) and propane (C₃H₈), their isotopic signatures (δ^{13} C and δ^{2} H for methane and δ^{13} C for ethane), hydrocarbon ratios, and the ratio of the noble gas ⁴He to methane in groundwater. For two out of three hydrocarbons the average concentrations in drinking water samples from relatively shallow bores (60-90 m depth) were significantly higher (six times for methane, 23 times for ethane) at distances < 1 km from gas wells (Figure 2-3). Based on the isotopic and hydrocarbon ratios, groundwater was found to be characteristic of a thermally postmature Marcellus-like source (the Marcellus Formation is the primary hydrocarbon resource ranging in depth from 1200-2500 m) in some cases (Figure 2-3). Jackson et al. (2013) hypothesise that the higher dissolved gas concentrations observed in drinking water are the result of (i) faulty or inadequate steel gas well casings and (ii) imperfections in the cement sealing of the annulus or gaps between casings and rock that keep fluids from moving up the outside of the gas well. Casing leaks can result from poor thread connections, steel corrosion, thermal stress cracking, and other causes (Wu et al. 2016). Once the protective steel casing breaks or leaks, stray gases could be the first indication of groundwater contamination; less mobile salts and metals from

formation waters or chemicals from hydraulic fracturing fluids can potentially arrive later. Cement seal failure may occur when cement shrinks, develops cracks or channels, or is lost in the surrounding rock formation during application (Jackson 2014). In case cement seal failure occurs in intermediate layers, the geochemical and isotopic compositions of stray gas contamination does not necessarily match that of the target gas, in which case no hydraulic fracturing chemicals or deep formation waters would arrive in shallow groundwater. Indeed, in such scenario a direct connection between the deepest formation layers and shallow aquifers does not exist.

While well integrity failure may be one plausible cause of groundwater contamination, there are two other potential mechanisms for contamination caused by hydraulic fracturing/horizontal drilling. These include enhancing deep-to-shallow hydraulic connectivity, and intersecting abandoned oil and gas wells (Jackson et al. 2013). Horizontal drilling and subsequent hydraulic fracturing can stimulate fractures or mineralized veins, increasing secondary hydraulic connectivity. The upward transport of gases is theoretically possible, including pressure-driven flow through open, dry fractures and pressure-driven buoyancy of gas bubbles in aquifers and water-filled fractures (Jackson et al. 2013 and references therein). Reduced water pressures after the fracturing activities could also lead to methane exsolving rapidly from solution and forming free a gas phase. If such free gas methane reaches an open fracture pathway, the gas should redissolve into capillary-bound water and/or formation water, especially at the lithostatic and hydrostatic pressures present at Marcellus Formation depths. Legacy or abandoned oil and gas wells (and even abandoned water wells) are another potential pathway for rapid fluid transport (Jackson et al. 2013).



Figure 2-3 (A) and (B) Concentrations of methane (A), ethane and propane (B) in drinking water wells vs. distance to natural gas wells. (C) Methane concentration plotted against δ^{13} C-CH₄, The grayscale shading refers to distance to nearest gas wells. (D) The ratio of ⁴He:CH₄ concentrations in drinking water wells vs. distance to gas wells (kilometres). The values are compared with water samples (mean ± SE) from the salt spring at Salt Springs State Park (n = 3) and Marcellus (n = 4) and Upper Devonian (n = 5) production gases (Jackson et al. 2013). Grey-shaded scale bars refer to (C) and (D) only.

Using numerical simulation models, Kissinger et al. (2013) tested under what circumstances several hypothesised flow paths for fracturing fluid, brine and methane would result into leakage of such fluids into shallower layers. The simulations used literature-based parameterisation (upper and lower bounds of hydraulic parameters) for potential hydraulic fracturing sites in Germany (North Rhine-Westphalia and Lower Saxony). Kissinger et al. (2013) considered three flow paths for hydraulic fracturing fluid and/or brine:

- Flow through natural fault zones (F1 in Figure 2-4): this involves fractures created during the stimulation period that could connect with a natural fault zone. As a result, the hydraulic fracturing fluid could be forced through this fault zone as a result of the strong pressure build-up in the system during hydraulic fracturing operations (considered to last for about 2 h in the study of Kissinger et al. 2013),
- Flow through leaky boreholes (F2 in Figure 2-4): fluids may leak into the freshwater aquifer through a borehole that experiences casing failure or cement seal failure,
- Spill at the ground surface (F3 in Figure 2-4): large amounts of contaminants may infiltrate into the aquifer in the case of an accident. A continuous contamination of the aquifer is also possible if a leak remains undetected.

Flow paths F1 and F2 are also relevant in case of methane (Figure 2-4); one additional flow path considers gas flow through rocks following gas mobilisation transport due to buoyancy. Flow path F3 has been previously been investigated as part of the Australian National Chemicals Assessment project (e.g. Mallants et al. 2017a), and will not be discussed any further here.



Figure 2-4 Possible flow paths of fracturing fluid, brine and methane into aquifers; see main text for definition of flow paths F1/M1, F2/M2, and F3/M3; F3 represents spill from a truck accident (Kissinger et al. 2013). Light grey coloures layers are low-permeable formations (aquitards); dark grey coloured layers are gas reservoirs or aquifers.

Three scenarios were numerically evaluated:

- Scenario 1: the short-term movement of hydraulic fracturing fluid or brine into the overburden (applied at the fault zone or intact overburden) induced by high pressures (50-700 bar overpressure) from hydraulic fracturing activities (a short-term high-pressure gradient is the driving force, while the pathway is a 30-m wide fault zone) (Figure 2-5),
- Scenario 2: the long-term (tens of years) horizontal and vertical movement of hydraulic fracturing fluid and brine along vertical fault zones connecting deeper aquifers (the contaminant source is assumed to be within in the groundwater after it escaped from the hydrocarbon reservoir, which in itself is an unlikely event) with shallower aquifers (a long-term natural hydraulic gradient is the driving force).
- Scenario 3: long-term (tens of years) methane gas migration from gas reservoir into fault zone owing to buoyancy and capillary forces.

Results for Scenario 1 show that the maximum vertical transport distance is limited to 50 m, and this is possible only if the permeability of the fault zone is 10^{-13} m² (about 10^{-6} m/s or 0.1 m/d) and an overpressure of 300 bar is applied

continuously for 2 hours (i.e. very conservative assumptions). For eight other parameter combinations, the vertical transport distance is much shorter or completely zero.



Figure 2-5 Schematic representation of the conservative assumptions made in Scenario 1 (Kissinger et al. 2013).

Simulations for Scenario 2 demonstrate that only under very conservative assumptions (hydraulic head difference between lower and upper aquifer is 60 m and fault hydraulic conductivity 10^{-13} m²) contaminants migrate up the fault and into the shallow aquifer, though concentrations are reduced by a factor 4,000 compared to the source concentration (discounting attenuation processes including degradation, sorption, hydrodynamic dispersion). Transport through the fault zone is effectively zero when its hydraulic conductivity decreased to 10^{-15} m² (about 10^{-8} m/s or 0.001 m/d). Kissinger et al. (2013) concluded that the conservative assumptions were still plausible for at least one of their study sites.

Results from Scenario 3 show that the leakage of methane into the shallow aquifer through the fault zone is only possible if all of the following conservative assumptions are met: (i) a permeable fault zone connecting gas reservoir with shallow aquifer, (ii) low residual gas saturation and low porosity, (iii) large volumes of methane mobilised from the gas reservoir, and (iv) a shallow gas reservoir (about 1,200 m). Kissinger et al. (2013) consider this a highly unlikely scenario.

Dusseault and Jackson (2014) investigated the possibility of hydraulic fracturing fluids moving upwards to shallow groundwater. They first discuss several factors that inhibit uncontrolled upward migration of induced fractures (based on horizontally drilled wells in shale gas reservoir):

- Production well construction: There is little chance of hydraulic fractures in the horizontal well section moving
 laterally and intersecting the vertical section of the wellbore a considerable distance away, and subsequently
 moving up along the wellbore (through the cement between casing and rock formation) during injection mainly
 because (i) the bottom part of the vertical production casing usually has a proper cement seal, (ii) the horizontal
 section of the well is drilled approximately parallel to the in situ minimum principal stress, therefore induced
 fractures propagate predominantly at 90° to the horizontal section, and (iii) the annular pressure on the
 production casing is monitored thus any breach in the production becomes manageable.
- Orientation of induced fractures: Hydraulic fracturing in zones where the minimum principal stress is horizontal will lead to induced fractures that will grow preferentially upwards, rather than being vertically symmetrical around the fracture point (Figure 2-6). Under such stress conditions, various US shales (e.g. Marcellus and Barnett shales) show maximum fracture growth height on the order of 600 m; beyond such vertical heights, natural fractures in the form of joints, faults, and bedding-plane partings stop vertical growth by allowing leakoff (i.e., fluid diversion) into multiple fractures.
- Imbibition of injected fluids and associated strain: Injected hydraulic fracturing fluids that do not return to the surface as flowback water or that are not trapped in open or half-open fractures in the shale gas reservoir will be

absorbed by the shale rock owing to strong capillary forces. Furthermore, hydraulic fracturing results in permanent volumetric strain of up to 30 to 50% of the volumes injected.

- Effect of uplift and surface erosion: In most parts of the world where sedimentary basins have been uplifted and subsequently eroded (all shale-gas basins identified to date are in uplifted, eroded basins), the stresses in the earth become redistributed. A typical situation is that where, at shallow depths, the vertical stress is the smallest of principal stresses, as a result, fractures will propagate horizontally. At greater depths, the stress condition becomes reversed, with the horizontal stress becoming the smallest, thus promoting vertical fracture propagation (Figure 2-7). For example, if a fracture is initiated in a horizontal well at a depth of 425 m (Figure 2-7), it will likely rise until it encounters the stress transition (stress turnover) zone where it will start to propagate horizontally and be more influenced by bedding. This stress condition provides a further barrier to the upward migration of fracturing fluids in most geological environments.
- Nature of the overlying strata: Low-permeability strata overlying shale gas reservoirs range from stiff naturallyfracture sediments to ductile fine-grained strata void of fractures. The former strata may have acted as a partial seal to upward fluid movement because the shale-gas reservoir is still intact. The latter formations are effective seals against fluid movement and insensitive to hydraulic fracturing occurring at much greater depths, i.e. they can experience a much larger strain before any fracture opening occurs. Furthermore, it is argued that it is extremely improbable that injection of large volumes of hydraulic fracturing fluid will cause any distortion of overlying strata that would lead to new pathways.
- Hydraulics of upward fracturing fluids migration to shallow groundwater: The scenario of upward fluid flow from
 a shale gas reservoir to shallow groundwater via pre-existing fractures as previously simulated by Myers (2012),
 was critically evaluated by Dusseault and Jackson (2014). The latter authors demonstrate the improbability of
 this scenario occurring because of hydraulic fracturing. On the basis of 'back-of-the-envelop' calculations they
 show that the additional pressure increment of 50 MPa applied at the ground surface by a fleet of fracking trucks
 is insufficient to lift fracking fluid to the shallow aquifer (a height difference of 1500 m was considered) in the
 short time provided. This conclusion is consistent with the observations that measured fracture-height growths
 never exceeded 600 m.
- Design of hydraulic fracturing stimulation: The large costs associated with hydraulic fracturing operations have resulted in highly optimised designs based on mathematical models and monitoring data. As a result, the actual fracturing zone, including the region of beneficial perturbation of the natural fractures, does not extend significantly beyond the top of the shale-gas target zone.
- Volumetric strain and fracture rise: Dusseault and Jackson (2014) argued that the concept of hydraulic fractures propagating in an uncontrolled manner toward potable water layers is not realistic. Their main argument is that to rise the fracturing fluid 1-2 km into a shallow aquifer, would require (i) injected fluid volumes orders of magnitude larger than what is being used, (ii) pumping for many days or weeks or even months, and (3) virtually zero leakoff to permeable zones. Furthermore, calculations suggest that the very small volumetric strains associated with depletion of pressure in the gas reservoir will generate only small strains in the overlying rock, insufficient to affect the natural fractures in those rocks.
- Production from shale-gas reservoir: Depleted shale-gas reservoirs become a zone of low regional pressure and are more likely to induce brine flow into it than to allow gas flow to escape. This physical reality was used by Dusseault and Jackson (2014) to conclude that the model assumptions (of sustained overpressuring during fracturing) used by Gassiat et al. (2013) in their simulations of leakage of fracturing fluids to a shallow aquifer were extremely unlikely in practice.

Based on the above arguments, Dusseault and Jackson (2014) conclude that the risk of hydraulic fracturing fluids or gas from the injection zone rising up into the intermediate zone during or after fracturing is remote. Furthermore, there is a strong economic incentive for operators to reduce the loss of injected fluids into non-productive overlying zones. As a result, the chances of dramatic fracture rise toward shallower depth and intersection with potable water aquifers, remote as they are, will become even lower as the companies perfect their techniques. Rare exceptions of contamination do exist,

unfortunately, such as that where hydraulic fracturing fluid was injected by mistake into a sandstone aquifer at shallow depth (136 m) whereas it should have been injected into the gas reservoir at 1500 m depth (Dusseault and Jackson 2014).

Dusseault and Jackson (2014) recognised that the seepage pathway of greatest risk for hydraulic fracture fluids are the decommissioned wells intersecting the hydraulic fracturing volume. Indeed, the most serious fluid communication risk during hydraulic fracturing is the possible intersection of the fractured zone with offset wellbores (e.g. old production gas wells) that pass through the stimulated rock volume created by the hydraulic fractures. If the quality of the cement and completion of such offset wells is poor, fracturing fluids that moved laterally to the offset vertical cased wells could then feasibly move upward along the annulus between the casing and the rock. Examples from inter-wellbore communication have been reported for the Barnett Shale of Texas (approximately 200 m distance between wells), Alberta (maximum distance up to 2400 m), and British Columbia (communication reported up to 4100 m distance). Dusseault and Jackson (2014) argued that the vast majority of communications involve pore-pressure pulses, not fluid breakthroughs. One exception involves a 80 m³ discharge of hydraulic fracturing fluid and formation fluid at the surface when a new well was fractured in Alberta, with 129 m between the offset well and the new well.

Dusseault and Jackson (2014) concluded that the migration of hydraulic fracturing or formation fluids (including natural gas) to the surface as a result of deep hydraulic fracturing of typical shale-gas reservoirs appeared most unlikely. They did recognise, however, that the real subsurface threat to shallow groundwater contamination was likely related to a combination of factors involving the characteristics of annular cement seals of production wells and the presence of natural gas in intermediate zones between shallow aquifers and the target shale-gas formations.



Figure 2-6 Hydraulic fractures tend to rise because of differential gradients; above the injection point, a positive driving force exists because the rock mass stress gradient (17-23 kPa/m) is larger than the fracturing fluid stress gradient (10-13 kPa/m). Below the injection point a pressure deficiency exists resulting in limited downward fracture growth (modified from Dusseault and Jackson 2014).



Figure 2-7 Relation between stresses and fracture orientation, north of Medicine Hat, Alberta, Western Canada sedimentary basin. At shallow depths (from 200 to approximately 380 m) the vertical stress is smaller than the minimum horizontal stress (referred to as reverse fault regime); as a result, fractures develop preferentially in horizontal direction. At depths below 380 m, a strike-slip fault regime exists (vertical stress is larger than minimum horizontal stress) promoting vertical fracture propagation (Dusseault and Jackson 2014).

The wellbore is identified as the most likely pathway of fluid leakage from depth to shallow aquifers, with methane gas as the principal fluid and buoyancy the main driving force. The principal pathways include the micro-annulus between the outermost casing and the debonded cement sheath and/or between the debonded cement sheath and borehole rock wall (Mueller and Eid 2006). Such gas seepage may become evident as surface-casing vent flow (SCVF) or as gas migration that occurs outside the casing strings. In Canada, surface-casing vents are left open to the atmosphere allowing the gas to vent freely. In the US, however, shutting-in surface and other casing-head valves is common practice. Gas migration may emit at ground surface or it may penetrate shallow aquifers leading to gassy water wells or groundwater contamination. Dusseault and Jackson (2014) argue that the potential for gas migration and subsequent groundwater contamination triggered by casing-head valve closure following gas release via the wellbore annulus after fracturing as reported by Bair et al. 2010).

Dusseault and Jackson's (2014) final conclusion on hydraulic fracturing risks was as follows:

- hydraulic fracturing itself appears not to present a significant environmental risk, except when abandoned or suspended well casings are intersected by fracturing fluids during the high-pressure stage of fluid injection. Likewise, producing wells situated in the same target formation as new wells involved with fracture stimulation may be affected by hydraulic fracturing fluids when the inter-wellbore distance is within approximately 250 m,
- the quality of cement completions of casing installations is a concern with regard to future gas migration. Indeed, gas migration outside the casing is typically a result of incomplete cementing (in the case of older conventional wells) or the formation of micro-annuli within or on the periphery of the cement sheath because of cement shrinkage. Gas-pressure gradients will promote the vertical ascent of gas slugs that will appear at the surface as pulsed gas flow. If such gas flows are not allowed to discharge to the atmosphere by shutting-in surface valves, potential for gas migration and subsequent groundwater contamination is exacerbated.

Engelder et al. (2014) analysed the hypotheses developed by Warner et al. (2012a) and concluded that these hypotheses (i.e. that hydraulic fracturing fluid migrates out of gas shale to contaminate groundwater) are highly unlikely for the following reasons:

- The near-total lack of free water in gas shale means that shale formations cannot feed a steady upward leakage of the kind proposed by Warner et al. (2012a). The highly water-unsaturated shales will function as a dehydrated sponge that sucks in any free water that comes in contact with the shales. Furthermore, the permeability of these water-unsaturated shale is orders of magnitude lower compared to that of a water-saturated shale, therefore it cannot sustain any appreciable water flow. Indeed, the permeability of any rock decreases by orders of magnitude as the water saturation decreases from unity.
- Because gas shale readily imbibes or takes up water, only a fraction of the injected hydraulic fracturing fluid is
 returned. The majority is retained within the shale due to processes of imbibition and diffusion-osmosis.
 Imbibition occurs within the silicate fraction of the shale which is water-wet; the kerogen fraction of shale is oilwet and hydrophobic and will not imbibe water.
- Coupled diffusion—osmosis processes and the forces associated with surface tension and adhesion (capillary forces) propel water into the matrix of gas shale and generate the high salinities observed in the recovered fracturing fluid (Figure 2-8). The contrast in water activity between brine and fresh water generates very substantial osmotic pressure differences that will drive hydraulic fracturing fluids into the shale matrix.
- The analysis of Warner et al. (2012a) was based on a single phase perspective, i.e. the interactions between the water phase and gas phase is not taken into account, while the analysis of Engelder et al. (2014) considered multiphase, capillary, and osmotic phenomena. Engelder et al. (2014) argued that leakage of water and gas along natural pathways from gas-filled shales like both the Marcellus and Haynesville was basically eliminated by capillary forces which act (and have been acting for over 200 My) as capillary seals. Importantly, hydraulic fracturing was believed not to change the capillary blockage.



Figure 2-8 Chemical and diffusion osmosis: transfer of water and inorganic ions between drilling fluid and formation when the drilling fluid is equal to the farfield formation pressure (Engelder et al. 2014).

In a review of well integrity across the conventional and unconventional gas industry in the US, Jackson (2014) illustrated the severity of well integrity failure, especially in Pennsylvania where, since 2005, the Department of Environmental Protection has confirmed more than 100 cases of well-related groundwater contamination. According to Jackson (2014), well integrity is the key to minimising many of the risks associated with hydraulic fracturing and unconventional resource extraction. Finally, Jackson (2014) identifies the need for much more information on the structural integrity of older producing wells and abandoned wells.

As part of a broader US EPA study (US EPA 2016a) on the relationship between hydraulic fracturing and drinking water, Reagan et al. (2015) carried out numerical simulations of water and gas transport between a shallow tight-gas reservoir (characterised by an ultralow permeability in the range of a nano-Darcy) and a shallower freshwater aquifer following hydraulic fracturing operations. Two general failure scenarios were considered in the simulations: connection between the reservoir and aquifer is assumed to occur (i) via a fracture or fault and (ii) via a deteriorated, pre-existing nearby well. The study uses generalized representations of single-well, single-pathway tight and shale-gas systems to identify the processes and parameters that could lead to rapid gas transport from such formations to groundwater resources. While Reagan et al. (2015) highlighted the need for additional research to better understand the risk from hydraulic fracturing, they argued that pathways created by hydraulic fracturing into pre-existing pathways cannot be discounted. Examples of the latter include naturally formed pathways (permeable fractures or faults) or artificial pathways (abandoned, degraded, poorly constructed, or failing wells). Reagan et al. (2015) also acknowledged that the possibility of human error in the construction and operation of wells cannot be ignored. Evidence for the existence, and their impact on groundwater, of such artificial pathways was provided by Dusseault and Jackson (2014), Jackson et al. (2013) and Jackson (2014). There is much less uncontested evidence that hydraulic fractures would connect into pre-existing natural pathways (faults, fractures); there is the recognition that strong upward gradients (considered unlikely) are necessary, along with permeable pathways, to drive upward migration. From their literature review, Reagan et al. (2015) concluded that few conclusions can yet be made about the parametric space under which fluids (gas and/or contaminated water) release can occur. Meaningful attempts to explore the parametric space that controls fluid release were reported by Kissinger et al. (2013) and Gassiat et al. (2013). The latter authors found that transport on thousand-year timescales may be possible under reasonable hydrologic conditions. Their conclusion was based on the simplified assumption of using a single-phase aqueous system to represent a shale system that is undersaturated. This analysis therefore ignores important capillary effects that would reduce the ability of the reservoir overpressure to drive aqueous flow.

Reagan et al. (2015) identified the following broad classes of plausible failure scenarios for upward migration of contaminants associated with hydraulic fracturing:

- Failure Scenario 1: Vertically extensive fracturing of the overburden/caprock/aquitard separating the hydrocarbon reservoir from overlying groundwater owing to inadequate design and/or operation of the fracturing operation (Figure 2-9a),
- Failure Scenario 2: Reactivation of dormant fractures/faults due to hydraulic fracturing creating pathways for contaminant leakage (Figure 2-9b),
- Failure Scenario 3: Fractures from the stimulation operation intercept older abandoned unplugged wells (e.g. conventional oil and gas wells) (Figure 2-10a),
- Failure Scenario 4: Continuous and highly permeable pathways via poorly completed wells due to inadequate design, installation or weak cement (Figure 2-10b).

By combining Scenarios 1 and 2 and 3 and 4 two general sets of failure pathways were considered in the simulations: faults/fractures and degraded wells (annular or tubular pathways). A separate study was carried out to explore the geomechanical reality of these scenarios and to determine if they are physically possible (constrained by the laws of physics and the operational quantities and limitations involved in hydraulic fracturing operations) (Kim and Moridis 2013). Geomechanical modelling and experimental studies generally agree that physical constraints on hydraulic fracture propagation will prevent induced fractures from extending from deep zones into drinking water resources (US EPA 2016a).

Key conclusions from the numerical simulations of failure Scenarios 1 – 4 are (Reagan et al. 2015):

• For the faults/fractures failure pathways, the most important parameters affecting gas transport towards a shallow aquifer (hydrocarbon reservoir-aquifer separation distances considered are 200 and 800 m) are the production regime (an active gas well mitigates gas release because rapid depressurisation of the small fracture volume counters the driving force for gas buoyancy and drives a downward flow of water from the aquifer via the connecting fracture which dissolved much of the gas that has escaped), fracture/faults hydraulic conductivity (which regulates the possibility of gas breakthrough), and separation distance (the greater the distance, the later the gas breakthrough time).

- For the degraded well failure pathways, most critical parameters are well conductivity and production regime. Well permeabilities smaller than 10⁻¹⁵ m² (about 10⁻⁸ m/s or 0.001 m/d), or a high-quality competent cement) do not result in any gas release when the separation distance is 200 m or larger. For separation distances of 800 m a producing gas well can mitigate gas migration for well permeabilities up to 10⁻⁹ m² (about 10⁻² m/s or 1000 m/d). Gas transport via well failure pathways allows for more amounts of gas release than via faults/fracture pathways.
- The amount of gas available for immediate migration toward the shallower aquifer is limited to that initially stored in the hydraulically induced fractures immediately after the conclusion of the stimulation process and prior to the beginning of gas production. In other words, any gas presence in the aquifer will be of limited duration.
- After the initial gas breakthrough has occurred, water flow is downward in nearly all parameter combinations considered. Note that the flow model assumes a hydrostatic initial pressure distribution; this is thus not an overpressurised hydrocarbon reservoir. A consistent downward trend in water flow was observed even when the gas well and water well were not in operation. Reagan et al. (2015) postulated that one mechanism responsible for a downward flow is the imbibition (i.e. absorption) of water into the undersaturated shale rock.

Reagan et al. listed the following assumptions and limitations for their numerical study:

- Neither the possibility nor the probability of occurrence of the failure scenarios are addressed, as there is yet insufficient data for such analysis.
- The identified hazards can only be put in the proper context once there is understanding about the relative probability of out-of-zone fracturing or fault activation versus interception of highly degraded, abandoned wells.
- Overpressurised hydrocarbon systems have not been studied and will likely result in different behaviour.
- The possibility or probability of continuous permeable fractures/faults has not been considered as it cannot be ascertained on current evidence.



Figure 2-9 Failure scenario 1 (a) and 2 (b) (Reagan et al. 2015).



Figure 2-10 Failure scenario 3 (a) and 4 (b) (Reagan et al. 2015).

US EPA (2016a) considered two major subsurface mechanisms by which the injection of hydraulic fracturing fluid and the creation and propagation of fractures can lead to contamination of drinking water resources, i.e. unintentional migration of fluids and gases (i) up the production well into groundwater owing to poor casing or cementing, and (ii) through subsurface geologic formations into a drinking water resource. Two main research questions were studied by US EPA to improve understanding of the possibility/probability and hazards associated with these mechanisms:

- 'How effective are current well construction practices at containing fluids—both liquids and gases—before, during, and after fracturing?'
- 'Can subsurface migration of fluids—both liquids and gases—to drinking water resources occur, and what local geologic or artificial features might allow this?'

In addressing the first question, US EPA reported that there are several examples where hydraulically fractured wells have or may have resulted in impacts to drinking water resources. Typical examples included: (i) an inner string of casing had burst during hydraulic fracturing, which resulted in a release of fluids on the land surface and possibly into the aquifer, and (ii) inadequately cemented casings that allowed methane migration through natural fractures and faults and contributed to impacts to drinking water resources (gas and other contaminants). US EPA further discussed the risks associated with fracturing older wells: they may not have been built or tested to the same specifications while exposure to aggressive conditions (high salinity, corrosive gases such as CO₂ and H₂S) will have contributed to casing degradation.

Answers to the second question included findings from both numerical modelling and microseismic studies, mostly based on a Marcellus-like environment. Results showed that fractures created during hydraulic fracturing are unlikely to extend upward from these deep formations into shallow drinking water aquifers (note the very large separation distances of up to a mile or more between hydrocarbon reservoir and aquifer). In other regions with much shallower shale, the depth of hydraulic fracturing would be between 30 – 579 m below the surface. A more likely scenario where migration of fluids to drinking water resources may occur is where oil and gas resources co-exist with drinking water resources. Currently the overall frequency of occurrence of this practice appears to be low. An even more likely scenario is that where liquid and gas movement from the hydrocarbon production zone to drinking water resources occurs via other production wells or injection wells near hydraulic fracturing operations. In Oklahoma, the likelihood of such well communication ('frac hits') was less than 10% between wells separated by more than 1,219 m, but increased to nearly 50% between wells less than 305 m apart. Surface spills from well communication incidents have been documented in the literature, which provides evidence for occurrence of frac hits (US EPA 2016a).

If offset wells are not able to withstand the stresses applied during the hydraulic fracturing of a neighbouring well, certain well components may fail (typically the cement components), which could result in a release of fluids at the surface. The US EPA has identified incidents in which surface spills of hydraulic fracturing-related fluids were attributed to such well communication events. Finally, the greatest potential for impacts is likely to be due to older or inactive wells—including oil and gas wells, injection wells, or drinking water wells—near a hydraulic fracturing operation (US EPA 2016a).

The US EPA (2016a) study concluded that it is important to note that the development of one pathway within a typical reservoir/caprock/aquifer system does not necessarily result in an impact to a drinking water resource. For instance, if an undetected fault would be intercepted by a gas production well, intact cement within the production well could keep fluids from migrating up along the well to the fault and still protect drinking water resources.

2.1.1.2. Summary of review findings from Australian studies

The US EPA (2016a) study, discussed in Section 2.1.1.1, provided a systematic analysis of likely failure pathways with a focus on unintentional migration of fluids and gases (i) up the production well into groundwater owing to poor casing or cementing, and (ii) through subsurface geologic formations into a drinking water resource. These are considered to be the two major subsurface mechanisms by which the injection of hydraulic fracturing fluid and the creation and propagation of fractures can lead to contamination of drinking water resources (US EPA 2016a). To date, a similar study has not been undertaken in Australia.

The next section provides a summary of literature on defective bores of any kind, including coal exploration bores, older conventional oil and gas wells (some of which are converted to water bores), or older water bores, that can potentially provide pathways for contaminants to reach groundwater receptors and/or receptors at the surface. The summary starts with a discussion on connectivity between coal seams and aquifers provided by the hydraulic fracturing process itself.

Hydraulic fracture growth

Hydraulic fractures can grow vertically from coal seams into the overlying and underlying rock layers. For such inter-layer fracture growth to occur, the minimum horizontal in-situ stress must be less than the vertical stress, and rock modulus and in-situ stress contrasts must be low enough to allow fracture height growth. Current understanding suggests that height growth will be retarded by the interactions that occur as the fracture grows into such a layered sequence. Jeffrey et al. (2017a) studied hydraulic fracture height growth into multiple rock layers of different in-situ stress using a 2D hydraulic fracture model that prescribed a constant pressure condition at the injection point. This pressure condition allows rapid height growth to occur when the stress and modulus conditions in the layers favour vertical growth. When vertical growth is favoured, the 2D model may predict rapid growth, which can lead to very large fluid flow rates. These flow rates or fluid fluxes can exceed physically possible limits. By including a fluid flux limit in the model, Jeffrey et al. (2017a) avoided unrealistic rates of fracture height growth. The results of the 2D model study demonstrated that sufficiently thick highstress layers lead to halt the fracture growth. Growth can occur through thin high stress layers, especially when the fracture length is relatively large when encountering the high stress layer. Because no lateral growth is allowed, the 2D model results represent the upper limit for vertical (height) growth, for both final extent and rate of growth. When lateral growth was included into the calculation using a P3D hydraulic fracture design model, the height growth was significantly reduced compared to the 2D model results. Jeffrey et al. (2017a) attributed this smaller height growth to the P3D model allowing the fracture to grow in length (lateral growth) as well as in height (vertical growth).

Findings from a recent review of fracture growth and well integrity by Jeffrey et al. (2017b) include:

- Hydraulic fracture growth in coal and growth in height into layers above and below a coal seam are affected by the rock properties and in-situ stresses. Interactions with bedding planes, faults and natural fractures often strongly affect the fracture growth.
- The nature and size of the fractures formed by coal seam gas stimulations are fairly well characterised because many have been mapped after mining, both in Australia and in the US. The fractures contain branches and offsets and sometimes form as T-shaped geometries with a large horizontal fracture overlying a vertical one.
- Monitoring of fracture growth by microseismic and tiltmeter instrumentation, and by using tracers, is important during early phases of development of new areas. This monitoring serves to calibrate modelling and verify that designs are producing the fractures intended. There is a gap in monitoring which would be filled by development of lower cost but reliable fracture monitoring methods.
- The wellbore provides a possible pathway along which fluids can move between zones in a coal seam gas well or from the subsurface to the surface. Application of correct drilling and completion practice effectively limits the risk of such fluid movement. Overseas studies indicate that well integrity may be a general problem, reinforcing the idea that the wellbore is the main risk of a leakage pathway developing between the reservoir and aquifers and the surface. Statistical data describing historical Australian coal seam gas well integrity experience were not found.
- Plugging and abandonment procedures must be designed and carried out using good engineering practice. Preexisting wells and boreholes that have not been plugged correctly pose a risk for vertical fluid movement and gas entering aquifers or venting at the surface.

The National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia (the National CSG Chemicals Assessment project) has carried out a screening level assessment of potential risks to human health and the environment

associated with surface-related exposure pathways of chemicals used in drilling and hydraulic fracturing⁴. This includes surface water, soils, and shallow unconfined groundwater systems. While the approach is consistent with previous US EPA assessments (US EPA 2004a, 2010, 2011), the National CSG Chemicals Assessment project did not examine the risks posed by chemicals to deeper groundwater systems such as confined aquifers⁵.

Therefore, the current review will focus on the limited number of studies that address bore and well integrity in Australia. In this way, evidence is collated regarding at least one of the likely failure pathways identified by US EPA (2016a), i.e. unintentional migration of fluids and gases up the production well into groundwater owing to poor casing or cementing. Whether or not the second failure pathway identified by US EPA (2016a) – unintentional migration of fluids and gases through subsurface geologic formations into a drinking water resource – is physically possible under typical Australian CSG operations will be addressed in the current study (Section 2.6).

Oil and gas well integrity failure

Poor well integrity is a considerable issue in oil and gas production operations (We et al. 2016). A number of studies have been carried out which indicate that there is not full integrity in a significant percentage of all wells. Since the CSG industry in Australia is relatively young (from middle 1990s), publications on CSG well failure have been quite scarce. Wu et al. (2016) have carried out a review of well failure rates reported in open international literature for conventional onshore oil and gas wells and some of CSG wells in North America and Scandinavia. One study on onshore gas well integrity in Queensland is included in their review (see further).

Because conventional oil and gas and shale gas wells are drilled to much greater depths than CSG wells, they are subject to higher temperatures and pressures and have more casing layers. As a result, their failure rates are expected to be higher than for CSG wells. Therefore, extrapolation of findings from overseas studies to Australian conditions with generally relatively shallow wells (typically 350 – 1,000 m) has to be done with great care. Nevertheless, the findings from conventional oil and gas and shale gas wells are useful in gaining understanding of possible failure mechanisms potentially relevant to CSG wells, and for obtaining upper bound failure rates.

CSG well integrity failures in Queensland

To date, there have been few estimates made of failure rates for CSG wells in Australia. From 2010 to March 2015, 6,734 CSG exploration, appraisal and production wells had been drilled in Queensland. The GasFields Commission Queensland (2015) reports statistics from well integrity compliance auditing undertaken during this period. This involved both subsurface gas well compliance and surface well head compliance testing on a subset of the wells drilled. For the subsurface equipment, no leaks were reported while there have been 21 statutory notifications (a rate of 0.3%) concerning suspect downhole cement quality during construction. After remediation, the cement failure rate was determined to be 0%. For subsurface equipment, the conclusion is that the risk of a subsurface breach of well integrity is assessed to be very low to near zero. In regards to the surface well head leaks, 199 leaks have been reported and have been subsequently fixed. This reporting is consistent with recent research which found that small 'equipment leaks' were relatively common (and often easy to repair) (Day et al. 2014).

Due to lack of comprehensive estimates of well integrity failure rates in Australia, one might be tempted to extrapolate estimates from other studies involving well failure rates for CSG wells or conventional oil and gas wells. Estimating CSG well failure rates from failure rates reported for conventional onshore/offshore oil and gas wells or from shale gas wells has to be done with care. Because offshore oil and gas wells are drilled in a different and more difficult environment than onshore CSG wells, their failure rates are expected to be much higher than for CSG wells. Furthermore, CSG wells are shallower than conventional oil and gas and shale gas wells, and therefore subject to lower temperatures and pressures.

⁴ <u>http://www.nicnas.gov.au/communications/issues/fracking-hydraulic-fracturing-coal-seam-gas-extraction</u>.

⁵ http://www.nicnas.gov.au/communications/issues/fracking-hydraulic-fracturing-coal-seam-gas-extraction/information-sheet.

Also, operating pressures for CSG wells are lower and they have less casing layers (GasFields Commission Queensland 2015).

Water bore integrity

In establishing field monitoring methods and guidelines to determine water bore and CSG well integrity, SKM conducted an evaluation of the integrity of 10,318 water bores in the Surat Basin in Queensland using the NGIS (National Groundwater Information System) database (Commonwealth of Australia, unpublished report). Based on the optimistic life time of steel in water bores (i.e. 45 years), it was assumed in the unpublished report that the water bores constructed prior to 1955 will now have poor integrity (1,893 bores), i.e., they have experienced well failure. This means that hydrological breach and production breach could occur in the old water bores allowing fluid movement between different geological units (if the bore penetrates multiple aquifers) and/or between the bore and surrounding geological units. This assumption is based on the fact that prior to 1955 nearly all of the water bores would have been constructed using steel casing. The water bores constructed between 1955 and 1967 were also considered to have poor integrity (1,668 bores), i.e. well failure is implied on the basis that the steel casing from prior to 1968 would be significantly corroded by now. It was further assumed that the bores using PVC or plastic were considered to have an increased likelihood of good (casing) integrity at present time since PVC does not corrode (but can degrade slowly over time), although good casing integrity does not necessarily lead to good bore integrity since fluid can still migrate behind the casing if the casing external annulus was not cemented or the cement sheath had poor integrity.

Estimated water bore integrity failure rates should not be extrapolated to coal seam gas wells. For example, the cement and casings may be different for water bores and CSG wells (NUDLC 2012; DNRM 2013a); also, prior to the late sixties cementing was not a requirement for water bores. Because cement plays a critical role in protecting steel casing from corroding, it has a significant impact on well life expectancy.

Coal exploration bores in Surat and Bowen Basins, Queensland

In Queensland, coal exploration bores probably represent the highest risk in providing significant pathways for interconnectivity between coal seam formations and aquifers, mainly due to their abundance and possible lack of appropriate decommissioning, both of which are at this stage unquantified (Wu et al. 2016). It has been estimated some 30,000 coal exploration bores have been drilled in the Surat Basin, with another 100,000 in the Bowen Basin (Free 2013, pers. comm., 28 February 2014). It is unknown however how many of these bores were decommissioned or, if they were decommissioned, the standard of the decommissioning work (Commonwealth of Australia 2014a).

Gas blowouts in Surat and Bowen Basins, Queensland

A review of gas blowouts in the Surat and Bowen basins, Queensland, has been provided by Wu et al. (2016). The blowout from a CSG well in the Daandine field (Surat Basin, South West Queensland) is a recent example of gas blowout widely reported in the media and well documented by DNRM (2011). This time, the blowout was from a CSG well that had been drilled (but suspended) in 2009 with well completion being undertaken in 2011. The well was capped after drilling and the blowout occurred when the well was being prepared for installation of a pump for production. After initial checks, the well was uncapped in order to install the pump. Before this could occur, water and gas began to flow to surface with increasing intensity. The blowout lasted for more than a day and spew methane and water up to 15 metres high before the well was secured by using heavy drilling mud. It appeared that the water level in the well had dropped to a point such that the pressure in the coal seam allowed the gas to desorb and flew into the well. It was reported that the owner of the well actually pumped some water into the well prior to uncapping it. It was not known if a blowout preventer was installed on the well, as this is a mandatory requirement by the Code of Practice for Constructing and Abandoning Coal Seam Gas Wells (DNRM 2013). This scenario is similar to a gas kick in conventional oil and gas well drilling. The gas in the well would need to be circulated out of the well under a controlled way.

While gas blowouts are some of the more spectacular examples of CSG well failure, they are very rare. While there have been 6,734 CSG exploration, appraisal and production wells drilled in Queensland from 2010 to March 2015, the blowout in the Daandine field is the only reported case in Queensland for the same period. In New South Wales, one blowout was recorded in 2011 (Parliament of New South Wales 2011). Finally, CSG operators are required to install blowout preventers to CSG well heads to prevent the uncontrolled release of water and gas from a well (NSW Petroleum (onshore) Act 1991; DNRM 2013).

Casing failure induced by hydraulic fracturing

High pressures associated with hydraulic fracturing operations can damage the casing and lead to breach of the interaquifer seal. The casing string through which fracturing fluids are pumped is subject to higher pressures during fracturing operations than during other phases in the life of a production well. To withstand the stresses created by the high pressure of hydraulic fracturing, the well and its components must have adequate strength and elasticity. If the casing is not strong enough to withstand these stresses, a casing failure may result. If undetected or not repaired, casing failures will serve as pathways for fracturing fluids to leak out of the casing (Wu et al. 2016).

A casing collapse was experienced when a rapid depressurisation of a wellbore occurred while completing a CSG well in Scotia field, Queensland (Johnson et al. 2002). This was immediately following a hydraulic fracturing operation to stimulate the coal seams. The field is known to have a highly deviatoric in-situ stress field, i.e., the difference is large between the maximum and minimum principal in-situ stress magnitudes. It was observed the BHTP (bottom hole treating pressure) was high, indicating the fractures created in the coal seam was complex. It was believed that during the treatment, any shear and conjugate shear sets of fractures within the coal seams were dilated and propped open by the treatment inducing quite large deformation in the coal. The rapid reduction in wellbore pressure resulted in parting of the casing and downhole assembly.

Fugitive emissions from CSG equipment and well casings

Recent reports from the US have suggested that fugitive emissions from unconventional gas production, especially shale and tight gas, are much higher than previously estimated. However, because of significant differences in production methods and other factors, it is unlikely that emission estimates from US shale and tight gas production are indicative of emissions from Australian CSG operations. To provide quantitative information on emissions from CSG operations, CSIRO and the federal Department of the Environment initiated a project to measure emissions from a range of production wells in Queensland and NSW (Day et al. 2014).

Methane emissions were measured at 43 CSG wells – six in NSW and 37 in Queensland (Day et al. 2014). Measurements were made by downwind traverses of well pads using a vehicle fitted with a methane analyser to determine total emissions from each pad. In addition, a series of measurements were made on each pad to locate sources and quantify emission rates. Of the 43 wells examined, only three showed no emissions. The remainder had some level of emission but generally the emission rates were very low, and much lower than those reported for US unconventional gas production (Allen et al. 2013). The principal methane emission sources were found to be venting and operation of gas-powered pneumatic devices, equipment leaks and exhaust from gas-fuelled engines used to power water pumps. Several of the larger equipment leaks were found at seals on water pump shafts on some wells. Once identified, well maintenance staff were able to repair some of these leaks on site, which effectively eliminated methane emissions. During the field measurements, no evidence of leakage of methane around the outside of well casings was found at any of the sampled wells. This reporting is consistent with surface well head leaks reported by the GasFields Commission Queensland (2015).

Day et al. (2014) emphasise the small sample examined during their study; therefore the failure rate of 93% (based on well pad gas emissions) may not be truly representative of the total well population. They further highlight that emissions may vary over time, for instance due to repair and maintenance activities. To fully characterise emissions, a larger sample size would be required and measurements would need to be made over an extended period to determine temporal variation.

Based on a much larger well population of 6,734 CSG wells (exploration, appraisal and production), the GasFields Commission Queensland (2015) identified 199 surface well head leaks, or a rate of 2.9 %.

Migration of fluids and gases through subsurface geologic formations into a drinking water resource

While many of the US based studies focus on potential pathways through faults and fractures, there is much less focus on pathways created by hydraulic fracturing that could allow contaminated fluids to migrate into water bores co-located in the same formation as the gas well. This is not a surprise as the shale gas formations have much higher salinity than the Australian CSG coal target formations, and are therefore not readily suitable for stock, irrigation or drinking water production. In Australia, however, the Walloon Coal Measured in the Surat Basin and the Bandanna formation in the Bowen Basin have a significant number of water bores co-located with CSG wells (Navi et al. 2015). For example, with 1,647 groundwater bores, the Walloon Coal Measures is the source of water for stock, domestic, industrial and urban purposes (OGIA 2016). Likewise, in the Bandanna Formation there a further 103 groundwater bores (OGIA 2013). As can be seen in Figure 2-11, several of such water bores are in relatively close proximity to CSG wells.

Other – natural – pathways for fluid migration may exist where the coal target formation discharges into springs or alluvial aquifers. For instance, the Condamine Alluvium is hydraulically connected to the Walloon Coal Measures with hydraulic gradients pointing from the coal formation towards the alluvium (Navi et al. 2015).

Wu et al. (2016) developed several conceptualisations of preferential flow pathways for use in local-scale and regionalscale groundwater modelling. Major pathways for movement of groundwater between strata have been identified and have been linked to failure of:

- uncased exploration bores backfilled with rock material upon decommissioning,
- cemented production wells plugged with cement cores upon decommissioning,
- wellbores during hydraulic fracturing,
- oil and gas wells repurposed for water extraction and water bores in which casing has corroded and/or there is no cementing of the annulus.

These conceptualisations were subsequently used in a simulation study to explore under which circumstances, if any, such preferential flow would cause significant impact on the groundwater water balance (Doble et al. 2016).



Figure 2-11. Locations of CSG wells (blue dots), groundwater bores not screened in the Walloon Coal Measures (white dots) and water bores screened in the Walloon Coal Measures (red dots) in a CSG field, North East Roma, Queensland. The width of the image is approximately 86 KM. Data obtained from Queensland Government database

(http://qldspatial.information.qld.gov.au/catalogue/custom/search.page?q=%22Coal%20seam%20gas%20well%20locations%20-%20Queensland%22). Accessed in August 2015.

2.1.2. Hazard screening approaches

DMP 2013

Hazard identification of products and chemicals is the first step in the risk identification process. The Department of Mines and Petroleum of Western Australia (DMP 2013) considers a product, chemical or substance to be a hazard if:

- it meets health hazard criteria;
- it meets environment health hazard criteria;
- it has specifically been identified as a pollutant, contaminant or a hazardous good under Western Australian or Australian legislation or regulations.

Health hazards:

Health hazards related to chemicals include:

- acute toxicity: adverse health effects to humans following short-term exposure to a chemical or substance;
- chronic toxicity: adverse health effects to humans following long-term exposure to a chemical or substance.

Acute toxicity refers to the adverse effects of exposure to a product or chemical over a short period of time (usually less than 24 hours). Acute toxicity effects can result in lethal or sub-lethal effects (e.g. irritation) to humans. As a minimum requirement in chemical disclosure, DMP requires human health acute toxicity data for all products using LC50 or LD50 data (as appropriate). LD50 or LC50 data for each product or chemical should be compared to the criteria for determining whether it is 'harmful', 'toxic' or 'very toxic' (examples provided in DMP 2013).

Chronic toxicity refers to the adverse health effects caused by repeated exposures to chemicals, often at low doses, over prolonged periods (i.e. months to years). The chemical does not necessarily have to exhibit acute toxicity to cause chronic toxic effects to human health or the environment. Chronic toxicity methods are based on guidelines from the Organisation for Economic Cooperation and Development (OECD) which mostly use toxicological studies on proxy species, such as rats and mice over their lifespan, to give an indication of potential carcinogenic, mutagenic, reproductive or developmental effects. The most widely used classification system for carcinogens and examples has 4 classes of carcinogen classification: Group 1 (known carcinogen to humans, Group 2a (probably carcinogenic to humans), Group 2b (possibly carcinogenic to humans (suggestive evidence), and Group 3 (unclassifiable as to carcinogenicity in humans (inadequate information)).

Environmental hazards: environmental hazards in relation to chemical use include:

- acute aquatic toxicity: adverse effects to marine or freshwater flora or fauna health following exposure to a chemical or substance;
- chronic aquatic toxicity: adverse effects to marine or freshwater flora or fauna health following exposure to a chemical or substance;
- bioaccumulation;
- persistence.

Acute aquatic ecotoxicity methods are based on guidelines from the Organisation for Economic Cooperation and Development (OECD), which mostly use toxicological testing on indicator aquatic species, such as fish, crustacea and macroalgae, to give an indication of relative toxicity to the aquatic environment. LC50 or EC50 data for each product or chemical should be compared to the criteria for determining whether it is 'harmful', 'toxic' or 'very toxic' (examples provided in DMP 2013).

Chronic aquatic toxicity data for aquatic organisms are generally less available than acute toxicity data and the range of testing procedures are less standardised (United Nations 2011). Common measures of chronic toxicity to aquatic organisms include the NOEC and EC₅₀ measures in accordance with OECD guidelines. NOEC or ECx data for each product or chemical should be compared to the criteria for determining whether it is 'harmful', 'toxic' or 'very toxic' (examples provided in DMP 2013).

Bioaccumulation refers to chemicals that remain in the environment for long periods of time and are capable of long range movement through the landscape (e.g. groundwater plumes, atmospheric dispersion, in organisms), building up in food chains and causing toxic effects. Bioaccumulation is best measured using intact organisms in the laboratory or in the field. It is usually expressed as the Bioconcentration Factor (BCF) or Bioaccumulation Factor (BAF), which represents the ratio of a chemical in an organism (e.g. tissue sample) to the concentration in the organism's environment (e.g. water). Bioconcentration factors show a correlation to the log of the octanol-water partition coefficient. The partition coefficient measures how hydrophilic or hydrophobic a chemical is and may be used to indicate those substances having significant potential to bioaccumulate. Hydrophobic chemicals with high octanol-water partition coefficients are preferentially distributed to lipids (fat cells) in animals, which tends to then bioaccumulate over time.

While BAF/BCF measures are preferred (BAF/BCF values \geq 1000 indicate the chemical is bioaccumulative; BAF/BCF values \geq 5000 indicate the chemical is highly bioaccumulative), the log octanol-water partition coefficient (log K_{ow}) can also be used to indicate bioaccumulation (log K_{ow} values \geq 4 indicate confirmed chemical bioaccumulation in aquatic environments). BAF, BCF and/or log K_{ow} data for each product or chemical should be compared to the respective criteria to confirm possible bioaccumulation.

Persistence refers to a substance's inability to degrade in the environment over time. Degradation often infers that the hazardous nature of chemicals will become less toxic over time compared to the parent chemical, but this is not always the case (e.g. polycyclic aromatic hydrocarbons (PAHs)). The absence of degradation processes results in chemical sinks in the environment and/or bioaccumulation (the gradual build-up of chemicals in plants and animals over time). Persistent chemicals in the environment may cause chronic health problems, particularly in higher order food chain animals and humans.

Commonwealth of Australia

In Australia several guidance documents are available on methods for assessing risks from use of industrial, agricultural and veterinary chemicals (EPHC 2009a, b; DoEE 2016a, b). The Approved Criteria for Classifying Hazardous Substances (Commonwealth of Australia 2004) provides the mandatory criteria for determining whether a substance is hazardous based on its human health effects, and optional criteria for determining whether a substance is hazardous based on its human health effects. These criteria are taken from Annex VI of EC Council Directive 67/548/EEC (as amended by Commission Directive 2001/59/EC of 6 August 2001).

Degradation threshold (half-life) data for each product or chemical should be compared to the criteria for determining chemical persistence (Table 2-2).

Medium	Degradation threshold criteria (half-life)	Method
Air	\geq 2 days	
Water	\geq 2 months	OECD Test Guideline 301 (freshwater)
		OECD Test Guideline 306 (marine)
Sediment	\geq 6 months	
Soil	\geq 6 months	

Table 2-2 Criteria for degradation threshold (half-life) for determining chemical persistence (EPHC 2009a, b; DoEE 2016a, b).

2.1.3. Risk assessments

There is an increasing awareness of the multiple potential pathways leading to human health risks from hydraulic fracturing. Setback distances are a legislative method to mitigate potential risks. Haley et al. (2016) attempted to determine whether legal setback distances between well pad sites and the public are adequate in three shale plays in the US. The authors reviewed geography, current statutes and regulations, evacuations, thermal modelling, air pollution studies, and vapour cloud modelling within the Marcellus, Barnett, and Niobrara Shale Plays. Evidence suggests that presently utilised setbacks may leave the public vulnerable to explosions, radiant heat, toxic gas clouds, and air pollution from hydraulic fracturing activities. Minimum setback distances range from 200 (Texas) to 500 (Colorado and Pennsylvania) feet (or 61 to 152 m). Their results suggest that setback distances in the USA may not be sufficient to reduce potential threats to human health in areas where hydraulic fracturing occurs. The study did not address drinking well, aquifer, and natural water contamination by formation fluids and hydraulic fracturing fluid.

In NSW, CSG exclusion zones are defined that prohibit CSG development in residential areas and future residential growth areas (DPandE 2014). Around such exclusion zones, CSG development is prohibited within a 2 km buffer zone. In Queensland a 200 m vertical depth setback has been defined for fracture stimulation within 2000 m of a water well (DEHP 2013). These restrictions prevent potential groundwater contamination or interference linked to fracture stimulation. A 2-km exclusion zone around towns with more than 1000 people was stipulated in Queensland's Resources Amendment Bill 2011, but lapsed in 2012 and was never enacted (Queensland Government 2014). Further details about CSG exclusion and buffer zones in other jurisdictions are available from NSW Chief Scientist and Engineer (2014d).

2.1.3.1. QGC 2012

Environmental risk assessment

As part of QGC's environmental risk assessment for its Southern, Central and Northern CSF fields in the Surat Basin, a conceptual site model was developed that provides the qualitative description of the plausible mechanisms by which receptors may be exposed to potential hazards (QGC 2012). Source-pathway-exposure mechanisms were evaluated for completeness by assessing:

- A potential hazardous chemical source.
- A mechanism for release of the chemical or hazard from the source.
- A pathway for the chemical or hazard to migrate to a potential receptor.
- Potential receptors of hazard.
- A mechanism for chemical or hazard exposure by receptors.

Hydraulic fracture design

QGC uses industry-wide acknowledged hydraulic fracture modelling software to predict fracture spread. Fracture geometries are modelled for all proposed activities to provide a high degree of confidence the fractures will remain within the Walloon Coal Measures (WCM). Typically fracturing of the WCM has an estimated fracture height range of between 0 to 40 m and an estimated average lateral extent of approximately 100 m.

Exposure pathways

QGC (2012) identified a number of potential surface and sub-surface exposure pathways for stimulation fluids to reach the receiving environment. Sub-surface pathways considered migration of hydraulic fracturing fluids or water with compounds derived from coal layers during the stimulation process into aquifers in the vicinity of the stimulation well:

- via new fractures developed during stimulation, leading to connection with the overlying Springbok Sandstone or underlying Hutton Sandstone;
- via pre-existing hydraulic continuity with the Springbok or Hutton Sandstone; and
- via leakage around the casing of the drilled well itself, into overlying aquifers, including near surface alluvial aquifers.

An assessment of these pathways concluded that, under most circumstances, such pathways will not exist. This is due to the standard procedure of developing the well soon after hydraulic fracture operation, thus causing groundwater and any hydraulic fracturing chemicals that have migrated away to flow back towards the CSG well and be captured at the surface.

Risk assessment findings

For the sub-surface pathway, the risk assessment has indicated low risk to health and environment for hydraulic fracturing chemicals used. Monitoring of water quality in the WCM aquifer was undertaken both pre- and post-fracturing as part of the risk assessment of hydraulic fracturing fluids. Ambient water quality in the WCM typically has salinity and metal concentrations in excess of ecological screening criteria. Following hydraulic fracturing, monitoring of wells targeting the WCM indicated increases in TDS, chloride, sodium, calcium, boron, sulfate, magnesium, manganese, zinc and phenol concentrations. The assessment concluded that the long-term changes in these parameters will not result in a change in classification of the water relative to the selected human health and ecological threshold criteria.

Due to the depth of stimulation activities in the WCM (greater than 400 m), limited coal thickness and extent, the estimated fracture height range of between 0 and 40 m and an estimated average lateral extent of about 100 m, and the stimulation fluid water quality, there is considered to be little risk of contamination of other formations and negligible risk of contamination of surface waters.

2.1.3.2. Santos 2014

Risk assessment process

Santos (2014) used a weight-of-evidence approach to evaluate the potential for human health and environmental risks as a result of its hydraulic fracturing processes for its GLNG project in the Surat and Bowen Basins, Queensland. In development of the risk assessment, the site setting, land use, hydrogeological conditions and beneficial uses of groundwater have been considered.

The risk assessment involved a systematic assessment of the toxicity of the chemicals used in hydraulic fracturing and the potential for exposures to humans and ecological receptors. During this process, key constituents of potential concern were identified and the effectiveness of exposure controls are considered. Through the process of evaluating potential exposure pathways, fate and transport modelling was also conducted to assess the mobility of chemicals within the coal seams. These components of work make up the qualitative component of the risk assessment.

On the basis of potential hazards identified in the qualitative risk assessment, and the potential for exposure to receptors identified in the exposure assessment, a quantitative risk assessment was conducted for human and ecological receptors (both terrestrial and aquatic). This quantitative risk assessment utilised methodologies outlined in the National Water Quality Management Strategy, National Environment Protection (Site Assessment) Measure (NEPM) and enHealth methodologies (enHealth 2012). This risk assessment methodology evaluated the potential risks posed by the combined mixture of chemicals and where flowback data was available, the combined risks posed by hydraulic fracturing chemicals and naturally occurring geogenic constituents.

Risk assessment findings

The weight-of-evidence approach used was based on a combination of methodologies and models to assess the fate and transport of chemicals and their associated risks.

The toxicity of the chemicals used in the hydraulic fracturing process were assessed for persistence, bioaccumulation and aquatic toxicity, terrestrial toxicity and human health toxicity. The assessment methodology determined that the chemicals used in hydraulic fracturing fluid operations can be generally characterised as non-hazardous with no high hazard chemicals identified in the semi-quantitative assessments. Overall the health concerns from these chemicals were limited with the primary concerns identified associated with potential risks to aquatic receptors.

The methodology incorporated an assessment of potential exposures to human and ecological receptors, with the following identified as the only potentially complete exposure pathways:

- Incidental ingestion and dermal contact by trespassers at well pads
- Livestock and native fauna exposure to flowback water (ingestion only) at the well pads
- Potential releases of water to aquatic environments.

Based on groundwater fate and transport modelling, no potentially complete exposure pathways were identified for groundwater. The solute transport modelling results suggest that organic chemicals of potential concern in the hydraulic fracturing fluid will be strongly attenuated within the coal seam, predominantly by adsorption. The extent of sorption of organic chemicals in aquifers depends on the content as well as nature of the organic carbon. The natural attenuation potential for organic chemicals within a coal seam is significantly higher than that of natural soils due to the high content of organic carbon (50-70%).

Furthermore, pathways to water bores co-located in the coal seam targets do not exist, since Santos GLNG's procedures for selecting locations for gas production wells would preclude installation of a production well in close proximity to an identified water supply bore. Also, Santos (2014) reported that there was no record of water supply wells screened within coal seams or in close proximity to Santos GLNG's petroleum lease areas.

Considering the hazard and exposure assessment and controls implemented by Santos GLNG, the overall risk to human health and environment associated with the chemicals involved in hydraulic fracturing was considered to be low.

2.1.3.3. Santos 2016

Risk assessment process

Santos GLNG has prepared a risk assessment of the chemicals proposed to be used in drilling fluids for natural gas extraction activities for its GLNG GFD Project Area located in south central Queensland, across the Bowen and Surat Basins (Santos 2016).

The risk assessment is based on the EPA-Expo-Box (US EPA 2016b) and the OECD Environmental Risk Assessment Toolkit (2014) which provide a compendium of risk assessment tools. These tools were used in the hazard assessment including preparation of the risk assessment dossiers (e.g., physico-chemical properties, environmental fate and transport parameters, ecological toxicological data, and mammalian toxicology data from databases linked to the OECD eCD eChemPortal) and in the exposure assessment to define default exposure parameters.

The risk assessment involved hazard characterisation, exposure assessement, and risk characterisation during different phases of the lifecycle cycle of products utilised in well construction and completion. The scope of the assessment was:

- The transportation of chemicals from the warehouse to the well lease;
- Activities associated with drilling fluid mixing and use at the well lease;
- Management, treatment and beneficial reuse during or after the completion of drilling activities at the well lease.

The steps in the hazard assessment combine the hazard identification and the hazard assessment process:

- Human health and environmental hazards.
- Persistent, Bioaccumlative and Toxic (PBT) assessment.

• Qualitative and quantitative assessment.

The exposure assessment comprised an evaluation of surface and subsurface exposure pathways and mass balance calculation to identify the amount of each chemical used in the process, and the estimated or actual potential exposure point concentration in the affected media (e.g., soil, groundwater, air). For the chemicals selected as constituents of potential concern (COPC), fate and transport modelling was used to characterise the degradation of chemicals over time and their potential transport (e.g., in groundwater) or partitioning into other phases. A highly conservative model of the fate and transport of key COPC with drilling fluid has been undertaken. Key constituents were identified based on their solubility mobility and toxicity to provide a broad spectrum of understanding of the potential area of groundwater impacts around a recently drilled well.

The final risk characterisation step included characterising environmental and human health risk, based on the identification of:

- Complete exposure pathways and hazard identification for each of the processes involving chemicals and exposure assessment;
- The level of risk for COPCs by exposure pathway, route, and cumulative;
- Uncertainty in quality and estimates of risk are included in the step.

Risk assessment findings

Based on an evaluation of the lifecycle of products and chemicals, environmental conditions in the areas of development, anticipated populations, and location, the following potentially complete exposure pathways were identified:

- Transportation of chemicals:
 - Human and ecological receptor exposure to chemicals as a result of accidental release during transport from supplier warehouse to well lease or within well lease and between well leases.
- Drilling and completion operations:
 - Human and ecological receptor exposure to chemicals as a result of accidental release during the storage and preparation of products on the well lease for drilling operations.
 - Human and ecological receptor exposure to residual chemicals (vendor chemicals and geogenic chemicals) in recovered materials as a result of an accidental release from storages (pits, storage tanks) on the well lease.
 - Human and ecological (terrestrial) receptor exposure to stored chemical products or residual material (including geogenic chemicals) in storages within the well lease.
- Treatment, recycling, disposal and beneficial reuse:
 - Human and ecological receptor exposure to residual chemicals in treated and reused waste materials during application as produced waters through irrigation techniques, or exposure to residual drilling material during land application or MBC activities.

The assessment showed there is no potentially complete exposure pathway to sources of drinking water; however, as a conservative measure, the theoretical concentrations for three exposure scenarios were compared to human health toxicity-based screening levels to screen for potential effects as a result of a release from the well lease that may migrate to groundwater used as a drinking water source. For five chemicals that exceeded the screening levels, the potential for these chemicals to migrate from the well lease to a landowner bore was evaluated using detailed fate and transport modeling.

A conservative groundwater modelling approach was conducted to assess the fate and transport of key chemical constituents in groundwater during the loss of drilling fluids, and the maximum lateral extent at which exceedances of risk-

based criteria could potentially occur. Based on the chemicals present within the drilling fluids, five COPCs had been identified for further evaluation via fate and transport modelling. These constituents were selected to represent the most mobile constituents (sodium and methanol) and other key constituents such as biocides used in the drilling fluid. They provide a broad spectrum of constituent physical properties that cover the range of potential mobilities associated with chemicals used in drilling fluids. The constituents considered include:

- Sodium or potassium (monovalent ions in salts)
- Methyl isothiocyanate (breakdown product of tetrahydro-3,5-dimethyl-1,3,5-thiadiazine-2-thione)
- Methanol
- Glyoxal
- Glutaraldehyde.

The conceptualisation for groundwater flow and solute transport simulations was based on a scenario where the drilling fluid was retained in the formation during drilling, and then dissolution occurred under natural groundwater flow conditions. A constant source of chemicals was released over the entire width of the receiving formation. The groundwater solute transport modelling indicates that under this highly conservative scenario the maximum lateral migration of constituent concentrations that may pose an unacceptable change in water quality is < 90 m in the Walloon Coals and the Sandstone Units. However, the modelled scenarios are based on large scale losses of drilling fluids to the formation (which rarely occurs).

2.1.3.4. US EPA 2016

Multi Criteria Decision Analysis (MCDA) Framework for Hazard Evaluation

US EPA (2016a) developed a Multi Criteria Decision Analysis (MCDA) Framework to combine various types of data that may provide insights on those chemicals that may be of greater concern than other chemicals to drinking water resources. The MCDA approach integrates factors related to hydraulic fracturing such as chemical toxicity, occurrence, and physicochemical data. The MCDA places the toxicity of hydraulic fracturing chemicals in the context of factors that may increase the likelihood of impacting drinking water resources. Each chemical was assigned three scores:

- a toxicity score;
- an occurrence score;
- a physicochemical properties score.

The three normalised scores (on a scale from 0 to 1) were summed (using equal weights) to develop a total composite hazard potential score for each chemical (on a scale from 0 to 3). These scores served as a relative ranking and a means of making comparisons across chemicals: scores mean chemicals that are predicted to have a higher likelihood to affect drinking water. These scores were not intended to define whether or not a chemical will present a human health hazard, or indicate that one chemical is safer than another. Rather, the scores served as a qualitative metric to identify chemicals that may be more likely to present an impact to drinking water resources, given available data on chemical properties and occurrence.

MCDA Results: Chemicals Used in Hydraulic Fracturing Fluid

The framework was applied to 42 chemicals used in hydraulic fracturing fluids and 29 chemicals detected in flowback and produced water that had sufficient information available for inclusion in noncancer MCDAs. Out of the first set of 42 chemicals, two (methanol and ethylene glycol) had previously been identified to be used in Australian hydraulic fracturing fluids (NICNAS 2017a). Two further chemicals (naphthalene and 2-methylphenol) have been selected from the second set

of 29, as they are considered in the current project (see Section 2.3) for proof-of-concept-testing. For these four chemicals the MCDA methodology is illustrated (Table 2-3).



Figure 2-12 Overview of the MCDA framework applied to the hazard evaluations (US EPA 2016a).

Table 2-3 MCDA results for selected chemicals used	in hydraulic fracturing fluid (HFF) and detected i	in flowback and produced water (FPW) (US EPA 2016a)
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Chemical	CASRN	Physicochemical properties score	Occurrence score	Toxicity score	Total hazard potential score
Naphthalene (FPW)	91-20-3	0.42	1.00	1.00	2.42
2-methylphenol (o-chresol) (FPW)	95-48-7	0.55	0.31	0.31	1.17
Methanol (HFF)	67-56-1	1.00	1.00	0.00	2.00
Ethylene glycol (HFF)	107-21-1	1.00	1.00	0.00	2.00

2.1.4. Chemical, biological, and geological attenuation

A detailed review about chemical, biological, and geological (adsorption) attenuation processes relevant for deeper groundwater pathways is available in Sections 4.2, 4.3, and 4.4.

2.1.5. Toxicity data and estimation methods

US EPA developed "estimation methods" such as the ECOSAR Class Program to predict toxicity values that can be used for hazard and risk assessment of new chemicals, i.e. to indicate which chemicals may need further testing or characterisation (Mayo-Bean et al. 2012). Such estimation methods are used to fill data gaps where little or no experimental measured data exists. The ECOSAR (ECOlogical Structure Activity Relationship) model and underlying methodology have been developed to screen chemicals in the absence of data. ECOSAR contains a library of class-based QSARs (quantitative structure activity relationship models) for predicting aquatic toxicity, overlaid with an expert decision tree for selecting the appropriate chemical class.

These approaches include nearest analogue analysis, chemical class analogy, mechanisms of toxicity, QSARs, and best professional judgment. In order to quickly complete an assessment for each new chemical, the US EPA now uses computerised QSAR models and expert systems to make estimates for physical/chemical properties, environmental fate, environmental toxicity, human health toxicity, and chemical releases and exposures in an effort to fill data gaps.

In the latest version of ECOSAR, the log Kow (octanol-water partition coefficient) values for each training set chemical is predicted using the KOWWIN program from U.S. EPA's EPISuite model (Meylan and Howard 1995).

ECOSAR derives toxicity values for three general types of chemicals:

- Neutral organics: alcohols, ketones, ethers, alkyl halides, aryl halides, aromatic hydrocarbons, aliphatic hydrocarbons, cyanates, sulfides, and disulfides
- Organic chemicals with excess toxicity: Some types of organic chemicals present a more specific mode of toxicity based on the presence of reactive functional groups acrylates, methacrylates, aldehydes, anilines, beta-diketones (linear forms), benzotriazoles, esters, phenols, aziridines, and epoxides.
- Surfactant (surface-active) organic chemicals: A surfactant is defined as a material that can greatly reduce the surface tension of water when used in very low concentrations.

2.2. Level-1 analysis: identifying chemicals of low concern

For the hazard screening framework to be cost-effective ('high-throughput'), a first step in the analysis must allow for chemicals with low hazard level to be excluded from more detailed analysis (which here includes pathway analysis and attenuation assessments).

The purpose of the Level-1 analysis is to efficiently identify i) chemicals of low concern not requiring any further detailed analysis, and ii) those chemicals that are not considered of low concern and thus require further analysis (at Level 2). The Level-1 analysis will consider existing lists and rules for screening chemicals and lists of chemicals previously screened to identify chemicals of low concern to human health⁶ and the environment⁷ (Table 2-4 and Figure 2-13):

- Chemicals previously identified by the National Assessment of Chemicals Associated with Coal Seam Gas
 Extraction in Australia as "of low concern" for human health (NICNAS 2017b) and shown to have a Tier 1 Risk
 Quotient < 1 for environmental risk assessment (DoEE 2017b), will be treated here also as "of low concern" for
 both human health and environment (and therefore not requiring the Level-2 analysis). Because exposure
 scenarios considered for deeper groundwater provide a higher degree of attenuation (i.e. lower predicted
 environmental concentrations) compared to the scenarios for surface handling, the latter scenarios are
 considered sufficiently conservative to not underestimate the impact in case of deeper groundwater scenarios.
 For chemicals previously identified as "of low concern" for *either* human health *or* the environment, the Level-2
 analysis is required here;
- For any chemical not previously tested (i.e. not listed by NICNAS (2017b)), the 'Level-1 analysis: Identification of chemicals of low concern' provides the means to carry out a simplified hazard screening and identify if such chemicals are of low concern or require further analysis. The 'further analysis' then involves consideration of exposure pathways and their likelihood, the expected travel times (indication of whether there is an immediate exposure or a potential delayed exposure) and the extent of attenuation processes that will reduce impacts (see further). The hazard screening methodology used within the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia (for human health and environment, see Table 2-4) is adopted here for the Level-1 analysis.

⁶ A chemical of low human health hazard and therefore inherently low concern for human health. Chemicals of low concern are considered to have a low likelihood of causing adverse human health effects should an exposure occur.

⁷ Chemicals with a risk quotient (RQ) < 1, where RQ = predicted environmental concentration/predicted no effect concentration.

Table 2-4. Summary of existing screening methodologies to identify chemicals of low concern for human health and environment

Step #	Screening process to identify chemicals of low concern for human health (NICNAS 2017b)	Step #	Screening process to identify chemicals of low concern for the environment (DoEE 2017b)
1	Comparison of coal seam gas chemicals with the existing national or international lists of substances considered to be of low concern (see Section 2.2.1 for further details)	1	Quantitative assessment when sufficient physico- chemical data is available to allow for modelling and calculations of the predicted environmental concentrations (see Section 2.2.2 for further details) Qualitative assessment, based on expert judgement
2	Series of validation rules to identify additional chemicals (including polymers) of low concern for human health (See Section 2.2.1.3, 2.2.1.4, and 2.2.1.5 for further details)		and weight of evidence, may be used for the risk assessment of those chemicals for which insufficient data is available for quantitative calculations (see Section 2.2.2 for further details)

When a site-specific assessment has to be undertaken, the DAF values can be used to derive predicted environmental concentrations for specific receptors provided an estimate of the chemical concentration at the source (the coal seams affected by the stimulation activity) is available.

2.2.1. Chemicals of low concern for human health per the National Chemicals Assessment

As part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia (the Assessment), NICNAS developed a method to screen the 113 drilling and hydraulic fracturing chemicals to identify those of low concern for human health (NICNAS 2017b). This method was based on that developed by NICNAS for the Inventory Multi-tiered Assessment and Prioritisation (IMAP) Framework (NICNAS 2015) independently of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia.

A single approach was utilised to screen both discrete chemicals and polymers to identify those chemicals and polymers used in coal seam gas extraction that are of low concern for human health. However, different validation rules were subsequently applied for each of these categories.

According to NICNAS (2017b), chemicals of low concern for human health are those considered to be of low likelihood of causing adverse effects upon exposure. The screening process to identify chemicals of low concern for human health involved six steps:

- Step 1: review of existing national or international lists of substances considered to be of low concern identified in the IMAP Framework;
- Step 2: analysis of these lists for their applicability for identifying coal seam gas chemicals of low concern for human health;
- Step 3: comparison of coal seam gas chemicals with the lists;
- Step 4: validation rules developed by NICNAS;
- Step 5: further validation rules, developed by NICNAS, based on expert judgement to identify additional coal seam gas chemicals of low concern for human health; and
- Step 6: validation rules to identify polymers of low concern for human health.

Each of the six steps is briefly discussed further in the subsequent sections.



Figure 2-13. Proposed Level-1 analysis to identify chemicals of low concern. RQ = risk quotient.

2.2.1.1. Step 1 and 2: Review of existing national or international lists of substances considered to be of low concern and analysis of lists for applicability for identifying coal seam gas chemicals of low concern for human health

NICNAS (2017b) reviewed six existing schemes used in Australia and overseas to qualify substances as of low concern for human health. From the six tools considered as being relevant, five were deemed applicable for identifying coal seam gas chemicals of low concern (Table 2-5).

Category	Identified schemes/lists	Used by NICNAS (2017b) to identify coal seam gas chemicals of low concern for human health
Lists of chemicals identified as safe with no condition of use	US EPA High Production Volume (HPV) Challenge Program Indicator 1	Yes
	European Union (EU) Regulation that deals with Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH) Annex IV	Yes
Lists of chemicals identified as low risk under conditions used	Inert Ingredients Eligible for US Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	Yes with validation (see below)
	US Food and Drug Administration (FDA) Generally Recognized as Safe (GRAS)	Yes
Lists of chemicals with reduced regulatory requirements based on their origin	REACH Annex V	Yes with validation (see below)

Table 2-5 Identified lists/groups for determining chemicals of low concern.

2.2.1.2. Step 3: Comparison of coal seam gas chemicals with the low concern chemical lists

The 113 chemicals reported to be used in drilling and hydraulic fracturing for coal seam gas extraction in Australia were compared with five of the lists identified in Table 2-5 Of the 113 chemicals, 38 were identified as potentially of low concern for human health based on their entries in these lists (NICNAS 2017b and Appendix 1).

NICNAS (2017b) considered that the uses of chemicals for extraction of coal seam gas in Australia may be different from those under which they have been considered low risk in other jurisdictions. Therefore, additional validation rules on chemicals identified by the FIFRA and US FDA GRAS lists were applied to ensure that coal seam gas chemicals that warranted more detailed assessment would not be simply classified as chemicals of low concern for human health (described below).

2.2.1.3. Step 4: Validation rules developed by NICNAS

The 38 chemicals identified as potentially of low concern for human health (see step 3) were evaluated against a set of validation rules previously developed by NICNAS for the IMAP Framework (NICNAS 2015). Chemicals meeting the following criteria were considered as requiring further assessment:

- chemicals identified as a concern or for which regulatory action has been taken overseas
- chemicals identified in international studies analysing blood in babies' umbilical cords
- chemicals meeting hazard criteria developed by NICNAS for use in the IMAP Framework based on any of the following sources:
 - Safework Australia's Hazardous Substances Information System (HSIS)
 - European Union (EU) Regulation on Classification, Labelling and Packaging (EU CLP; conversion of old EU classifications to adopted Globally Harmonised System of Classification (GHS)
 - International Agency for Research on Cancer (IARC)
 - National Toxicology Program Report on Carcinogens (NTP ROC)
 - US EPA Cancer Guidelines
 - American Conference of Industrial Hygienists (ACGIH) Categories
 - EU list of endocrine disrupters
 - List of neurotoxic chemicals from the Agency for Toxic Substances and Disease Registry (ATSDR).
- chemicals included in the Poisons Standard (the Schedule for Uniform Scheduling of Medicines and Poisons [SUSMP]) (TGA 2012) (except where the listing is in Appendix B of TGA 2012)
- chemicals removed from Annex IV of REACH as part of the review process
- strong or moderate acids and bases, quaternary ammonium salts, and anhydrous deliquescent materials.

2.2.1.4. Step 5: Further validation rules developed by NICNAS to identify additional chemicals of low concern for human health

An assessment of the chemicals internationally recognised as safe and/or of low risk (Step 2) enabled NICNAS to develop further validation rules (based on expert judgement) for identifying additional chemicals that may be considered of low concern for human health. These rules are described below.

Binary inorganics and organic acid salts

The hazard profiles of binary inorganics and salts of organic acids were characterised taking into consideration the separate toxicities of the anion and the cation components. The following anions, cations and organic acids were identified for potential inclusion in the list of chemicals generally considered of low concern:

• Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, CO₃²⁻, PO₄³⁻, NO₃⁻, OH⁻, O²⁻ and SO₄²⁻, and simple salts of acetate, citrates, lactates, tartrates, malates and di- and tri- phosphates.

This judgement was based on the occurrence of a number of such simple salts on the lists in Table 2-5, and the absence of classifications under Safework Australia's Hazardous Substances Information System (HSIS) for simple salts, except where these were classified for local irritant properties relating to acidity, basicity or desiccation.

Hydrates

As hydrates of a substance or hydrated ions are formed by association of a substance with water, the hydrates of chemicals considered as being of low concern for human health are themselves also considered as low concern for human health, as will hydrates where the anhydrous form is ruled out due to desiccation effects.

Naturally occurring substances

Naturally occurring substances – that is, unprocessed chemicals occurring in the natural environment – for which there are no known toxicological effects, such as nut hulls or wood dust, were also considered as substances or chemicals of low concern for human health.

However, it should not be assumed that dusts from these substances do not present a hazard to human health. High concentrations of dust in the workplace may cause unpleasant deposition of dust in the ears, eyes and upper respiratory tract. An exposure standard of 10 mg/m³, measured as inhalable dust (8 h time weighted average) has been assigned for such 'nuisance' dusts. This exposure standard for dusts not otherwise classified is only applicable when the particulate material does not contain other substances that may be toxic or cause physiological impairment at lower concentrations. In these circumstances, the exposure standard for the more toxic substance should be applied. For example, where a dust contains asbestos or crystalline silica, exposure to the materials should not exceed the appropriate value for these substances (Safe Work Australia 2012).

2.2.1.5. Step 6: Validation rules to identify polymers of low concern

Validation rules developed for discrete chemicals were considered inappropriate to be used for polymers. Therefore, an additional set of validation rules was developed to identify polymers of low concern. Validation for polymers involves a comparison of the polymers to the NICNAS' New Chemicals Program Polymer of Low Concern (PLC) criteria.

The PLC criteria used in the NICNAS New Chemicals Program are based on certain characteristics such as Number Average Molecular Weight (NAMW), proportion of low molecular weight species, Functional Group Equivalent Weight (FGEW) for reactive functional groups and the stability of the polymers (NICNAS 2013).

To apply this validation rule, reactive functional groups (RFGs) are identified in the polymers under consideration. These RFGs are then screened against the RFGs considered to be of low concern as described in the NICNAS Polymer of Low Concern (PLC) criteria. Polymers with RFGs other than those considered of low concern in the PLC criteria were assigned for further assessment by NICNAS (2017b). The following polymers were identified as being of low concern based on this additional set of validation rules: i) 2-propenoic acid, methyl ester, polymer with 1,1-dichloroethene, ii) Guar gum, carboxymethyl 2-hydroxypropyl ether, sodium salt, iii) 2-propenamide, homopolymer, iv) 2-propenoic acid, polymer with 2-propenamide, v) polyacrylamide/polyacrylate copolymer, vi) Polymer I (CBI), and vii) Polymer II (CBI).

2.2.2. Chemicals of low concern for the environment per the National Chemicals Assessment

The approaches used for the environmental assessments include a quantitative (deterministic) and qualitative approach (DoEE, 2017b):

- A quantitative (deterministic) approach was developed to assess chemicals for which sufficient physico-chemical data is available to allow for modelling and calculations of the predicted environmental concentrations that might occur as a result of release of the chemical under a variety of scenarios.
- A qualitative assessment approach, based on expert judgement and weight of evidence, may be used for the risk assessment of those chemicals for which insufficient data is available for quantitative calculations.

The quantitative and qualitative methods conform to Australia's national environmental risk assessment guidance manual (EPHC 2009a) and were informed by the principles outlined in Organisation for Economic Co-operation and Development [OECD (2014)] and the US Environmental Protection Agency's *Framework for ecological risk assessment* (US EPA 2014b). The US EPA Framework is based on principles described in a series of publications from the US National Research Council on scientific risk assessment methods (US NRC 1983; US NRC 1994; US NRC 2009).

2.2.2.1. Quantitative assessment approach

When sufficient physico-chemical data is available to allow for modelling and calculations of the predicted environmental concentrations that might occur as a result of release of the chemical, and suitable ecotoxicological data is also available, a quantitative environmental risk assessment can be undertaken. The quantitative environmental risk assessment undertaken as part of the National Chemicals Assessment uses the risk classification (i.e. the characterisation of the RQ) for each chemical in accordance with the principle outlined by EPHC (2009a) and ANZECC/ARMCANZ (2000) guidelines.

The deterministic assessment approach includes four main stages (DoEE 2017b):

- Stage 1: problem formulation identification of appropriate environmental compartments
- Stage 2: hazard and effects characterisation characterises the ecotoxicity of chemicals based on available data; calculate a predicted no effect concentration (PNEC) for the organism most sensitive to the chemical under consideration.
- Stage 3: exposure characterisation characterises the potential exposure of environmental receptors (such as an aquatic ecosystem) to a chemical if it is released into the environment. Use mathematical models are used to calculate the predicted environmental concentration (PEC) of the chemical in the relevant compartment. The scenarios under which chemicals may be released to surface environments by coal seam gas activities in Australia were investigated using a tiered process whereby the values used for modelling evolve from standard conservative values to more realistic values.
- Stage 4: risk characterisation quantifies and describes the environmental risk of a chemical used under specified scenarios. The PEC is compared with the PNEC to calculate a risk quotient RQ.

The classifications of risk for each chemical or chemical group assessed are:

- Chemicals with RQ < 1 are of "low concern", i.e. they are unlikely to have adverse environmental impacts if used in accordance with the assessment scenarios,
- Chemicals with ≥ 1 RQ < 10 are of "potential concern", i.e. further risk mitigation measures may be required if the chemical is used,
- Chemicals with RQ ≥ 10 are of 'potentially high concern', i.e. further risk mitigation measures are likely to be required if the chemical is used.

Where the National Chemicals Assessment screened out chemicals at Tier 1 (RQ < 1), the chemical is considered to be of low concern for the particular scenario assessed and not requiring further assessment. The Tier 1 assessment is conservative by design (e.g. uses bounding estimate values, and assumes that the coal seam gas working site is anywhere in Australia). Chemicals presenting a potential concern ($RQ \ge 1$) proceed to a Tier 2 assessment (DoEE 2017b).

The Tier 1 environmental risk assessment revealed that 3 chemicals showed RQs < 1: calcium chloride (CaCl2), ethanedial, and methanol (DoEE 2017b).

Note again that exposure scenarios considered for deeper groundwater provide a higher degree of attenuation (i.e. lower predicted environmental concentrations) compared to the scenarios for surface handling (considered in the National Chemicals Assessment). Therefore, the latter scenarios are considered sufficiently conservative to not underestimate the impact in case of deeper groundwater scenarios.

2.2.2.2. Qualitative assessment approach

When no suitable ecotoxicity data are available for quantitative risk assessment purposes, qualitative risk assessments may be used. Qualitative environmental risk assessments can be undertaken in accordance with the IMAP approach (NICNAS 2015) and the approach developed by Environment Canada (Environment Canada 2003). This approach is informed by intensive compilation, analysis and interpretation of the available scientific literature on each chemical.

The Environmental Risk Assessment Guidance Manual for Industrial Chemicals (EPHC 2009a) recommends the approach developed by Environment Canada (2003) for applying expert judgement to matters including:

- Creating a weight of evidence to support the selection of pivotal information.
- Qualitative analysis of degradation and persistence of chemicals.
- Qualitative analysis of bioaccumulation.
- Qualitative analysis of inherent ecotoxicity.
The Canadian approach to qualitative assessment of chemicals with limited data informed the methodology used in Australia to assess industrial chemicals under the Inventory Multi-tiered Assessment and Prioritisation Framework (IMAP). This Framework operates under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS 2015f).

Consistent with the deterministic approach, the risk classification for each chemical evaluated is determined in accordance with the principles outlined by EPHC (2009a) and the Australia and New Zealand Conservation Council Agriculture and Resources Management Council of Australia and New Zealand (ANZECC and ARMCANZ 2000a) guidelines. The classifications of risk for each chemical or chemical group assessed are:

- Chemicals of 'low concern': These chemicals are assessed to be unlikely to have adverse environmental effects if they are released to the environment from coal seam gas operations. Chemicals of low concern do not require specific risk management measures.
- Chemicals of 'potential concern': These chemicals have the potential to cause adverse environmental effects if they are released to the environment from coal seam gas operations. Specific risk management measures may be necessary to ensure that chemicals of potential concern do not harm the environment.
- Chemicals of 'potentially high concern': These chemicals are likely to cause adverse environmental effects if they are released to the environment from coal seam gas operations. Specific risk management measures are likely to be required to ensure that chemicals of potentially high concern do not harm the environment.

2.3. Selection of chemicals for proof-of-concept testing

2.3.1. Methodology

Representative chemicals were selected for assessment of attenuation and dilution from typical chemical groups (chemical indicators) if reliable data (or QSAR data) were available on i) physicochemical properties mobility (geological attenuation) and persistence (biological and chemical attenuation), ii) health effects and ecotoxicity, and iii) chemical use for CSG extraction in Australia. Sublethal toxicity effects of contaminants such as endocrine disruption are not considered in this study. Similarly, the effects of mixtures of contaminants are not considered as the ecotoxicological data to develop the required concentration additive models of mixture toxicity are not available.

The chemicals tested included the following (Table 2-6):

- Typical hydraulic fracturing and drilling chemicals:
 - chemicals that are unlikely to pose a risk of adverse health effects (long-term public exposure) based on NICNAS (2017b): *bronopol, methyl-chloro-isothiazolinone*
 - chemicals of potential concern (a potential risk of adverse health effects in case of long-term public exposure, NICNAS 2017b): *boron (boric acid, borax)*
 - chemicals that could not be assessed based on the Inventory Multi-tiered Assessment and Prioritisation Framework (NICNAS 2015): *limonene*
 - chemicals that represent an important group of polymers used in hydraulic fracturing and that are of low concern for human health (NICNAS 2017b) and the environment (DoEE 2017b): *acrylamide polymer*
- Explosives are used to obtain a pattern of perforations through the casing and cement sheath and into the productive formation to provide effective flow communication between a cased wellbore and a productive reservoir: HMX (*cyclotetramethylene trinitramine*) is commonly used for casing perforation (Hansen 2011).
- Geogenics: a small number of geogenics have been included to demonstrate the framework is sufficiently generic to include i) effects of anthropogenic chemicals on geogenic chemicals (mobilisation due to changes in redox, pH, EC); and ii) changes in solubility and mobility of geogenics due to interaction between degradation/transformation products and geogenics. Selected chemicals are: 2-methylphenol, naphthalene, uranium, arsenic, and barium.

Although a large number of cement chemicals/additives (typically set accelerators, set retarders, extenders, weighting agents, dispersants, fluid-loss control agents, lost circulation control agents, and other specialty additives are used for wellbore cement slurries) are used in preparing grout for the borehole cement sheath (Michaux et al. 1989), they would all have a very low mobility as they are incorporated in the cement minerals and thus part of a solid matrix. For this reason they were excluded from the hazard screening. Consideration has been given to the fact that the conditions of use of CSG chemicals in Australia may be different from those under which they have been considered low risk in other assessments, typically surface environments. Especially the conditions within deep groundwater, i.e. higher temperature, pressure, and salinity, anoxic, etc., are likely different from conditions considered to determine if chemicals are of low concern. Therefore, this study has tested chemical behaviour in deep groundwater as a means to identify if they are of low concern or warrant more detailed assessment.

The Level-2 analysis provides understanding about chemicals that is complementary to the "lists-and-rules" based analysis. This allows to verify one does not end up with false negatives or false positives as a result of the Level-1 analysis. However, this testing should be to check that the proposed process works as anticipated and should not be for hazard or risk assessment purposes.

Chemicals have been selected to mainly demonstrate the operability of the Level-2 analysis; some of these chemicals have been part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia or IMAP assessments, others have not been assessed previously. This study will not run any of the chemicals through the Level-1 "identification of chemicals of low concern" step, mainly because this study is not an assessment of the hazard or risk associated with specific chemicals. Demonstrating the Level-2 analysis, which involves pathway conceptualisation and analysis including travel time estimations and attenuation, is the focus of this study.

The Level-2 analysis may be used to confirm or validate chemicals identified as "of low concern", based on considering different pathways and exposure scenarios (typical of deep groundwater) than what would be considered under the Level-1 "identification of chemicals of low concern". This validation is appropriate because previous coal seam gas related assessments (DoEE 2017b, NICNAS 2017b) only considered surface environments (soil and surface water) and shallow groundwater, whereas deep groundwater conditions pose different biogeochemical conditions that may result in different attenuation, and possibly different pathways. Inclusion of these chemicals also allows for testing and validation of the deeper groundwater methods as, based on the conceptual model, it is considered unlikely that risk quotients will increase in deeper groundwater environments when compared to the shallow environments tested previously (NICNAS 2017b).

Note that the output of the Level-2 analysis is a Dilution Attenuation Factor – DAF (i.e. the reciprocal of concentration at the receptor for a hypothetical unit chemical concentration at the source), which allows ranking of the chemicals in terms of their potential for exposure and attenuation. Typically, chemicals with a high potential for exposure will have a low potential for attenuation; conversely, chemicals displaying a low potential for exposure likely have a high potential for attenuation.

2.3.2. Description of selected chemicals

2.3.2.1. 2-Methylphenol

Phenolic compounds such as phenol and 2-methylphenol have been observed in both low-rank and bituminous coals (Siskin and Aczel 1983) and these are likely to be derived from cleavage of aromatic compounds as well as transformation of plant cell walls under high pressure and temperature during coal formation. In the US phenolic compounds such as dimethylphenol have been detected in coal seam gas produced water in concentrations up to 5.89 mg/L (Orem et al. 2007). Phenol was detected at a level of 0.3 µg/L in Australian coal seam gas water holding ponds of the Walloon production area (Stearman et al. 2014). Specific drinking water guidelines for phenols currently do not exist (Orem et al. 2007; NHMRC and NHMMC 2011; WHO 2011). Therefore, the effect of chronic, long-term exposure to phenolic compounds is not well established. For the protection of aquatic life in freshwater ecosystems a threshold of 4.0 µg/L was recommended by the Canadian Council of Ministers of the Environment (CCME 1999a). For aquatic ecosystem protection (95% protection level) the Australia and New Zealand water quality guideline for phenol is 320 µg/L (ANZECC/ARMCANZ 2000).

2.3.2.2. Naphthalene

PAHs such as naphthalene belong to the naturally occurring compounds also known as geogenic compounds. Owing to their low water solubility (de Maagd et al. 1998), PAH contamination of water is generally considered to be of lesser concern. Nevertheless, they are of significance due to the known hazards, such as carcinogenicity, that they can present for human and environmental health (EC 2003). For aquatic ecosystem protection (95% protection level) the Australia and New Zealand water quality guideline for naphthalene is 16 µg/L (ANZECC/ARMCANZ 2000). Analysis of coal seam gas produced waters from the Powder River Basin (WY, USA) indicated PAHs were the most commonly observed group of organic compounds; total PAH concentrations ranged up to 23 µg/L (Orem et al. 2007). In a more recent study total PAH concentrations in coal seam gas produced water from the US were shown to exceed 50 -100 µg/L (Orem et al. 2014). Based

on 47 sampled wells of the Walloon coal seam gas production area, Stearman et al. (2014) reported only seven wells with detectable levels of PAHs, including naphthalene and phenanthrene. The maximum naphthalene and phenanthrene concentrations from a single well were 0.046 μ g/L and 0.02 μ g/L, respectively. Of all detected PAHs, naphthalene was detected at the highest concentration. Naphthalene was detected at a level of 0.06 μ g/L in Australian coal seam gas water holding ponds of the Walloon production area (Stearman et al. 2014).

No	Name	CAS Number	Group (class)	Reasons for selection	
1	2-methylphenol (o-cresol)	95-48-7	Phenol/cresols (Geogenic)	Identified based on previous work on Australian coal seams	
				Greater likelihood of detection	
				A toxic compound but no local water quality guidelines	
				Medium mobility and low persistence	
				Good data availability	
2	Naphthalene	91-20-3	PAH (Geogenic)	Naphthalene represents a broader class of polycyclic aromatic hydrocarbons which are an important class of geogenic compounds	
				Low mobility and moderate persistence	
				Good data available in literature	
3-5	Uranium, barium, arsenic	7440-61-1,	Inorganics/ radionuclides	Identified based on our previous work on geogenic contaminants release from	
		7440-39-3,	(Geogenic)	Australian coal seams. Arsenic is a contaminant of general of concern in groundwater systems. Uranium represents a common coal-derived radionuclide. Boron and Barium	
		7440-38-2		were detected at relatively high concentrations in the geogenic contaminants work.	
6	нмх	2691-41-0	Explosives	A nitroamine compound with interesting chemistry	
			(Drilling chemical)	Minerals may play a role in its mobility	
				Moderate mobility, high persistence	
7	2-butoxyethanol	111-76-2	Surfactant	Surfactant used as pre-flush hydraulic fracturing additive	
			(HF chemical)	Can be of concern in large, uncontrolled spills	
				Very similar properties to 1,2 ethanediol (ethylene glycol), CAS RN 107-21-1.	

Table 2-6. Chemicals selected for screening and attenuation analysis. NCA = National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia

			NCA (human health hazard screening): requiring	High mobility and low persistence
			further human health	Anaerobic patriway probable
			hazard assessment;	Some data available
			NCA (human health hazard	
			risk assessment): MOE	
			indicates the chemical is	
			unlikely to pose a risk of	
			adverse health effects to	
			workers (long-term	
			occupational exposure);	
			MOE suggests a potential	
			risk of adverse health	
			effects for long-term public	
			exposures in the absence of	
			standard risk managemetn	
			measures;	
			NCA (environment):	
			Assessed to be of low	
			concern for the	
			environment	
8	Bronopol	52-51-7	Biocide	Biocides – toxic by design – environment concern
			(HF chemical)	Of concerns to workers (if safeguards not in place)
			NCA (human health hazard	Very high mobility, moderate persistence
			screening): requiring	Bronopol transformation products (halonitromethanes) are more toxic
			further human health	
			hazard assessment;	Some data available
			NCA (human health hazard	
			risk assessment): MOE	

			suggests a potential risk of adverse health effects for workers in the absence of standard risk management measures; MOE indicates the chemical is unlikely to pose a risk of adverse health effects for long-term public exposures NCA (environment): no longer in use as of July 2015	
9	Methyl-chloro- isothiazolinone	26172-55-4	Biocide (HF chemical) NCA (human health hazard screening): requiring further human health hazard assessment NCA (human health hazard risk assessment): MOE indicates the chemical is unlikely to pose a risk of adverse health effects for long-term public exposures and to workers (long-term occupational exposure)	Represent thiazole biocides Used as a HF chemical for microbial control High mobility, high persistence in water Anaerobic degradation possible Model data available.
10-11	Boron (boric acid, borax)	10043-35-3, 1303-96-4	Gel management (HF chemicals)	Of broader interest as HF and geogenic category Recommended for further assessment (environment assessment – NCA) Boric acid high environmental concern in case of spill (NCA)

			Boric acid, borax: NCA		
			(human health hazard		
			screening): requiring		
			further human health		
			hazard assessment		
			Boric acid, borax: NCA		
			(human health hazard risk		
			assessment): MOE indicates		
			the chemical is unlikely to		
			pose a risk of adverse		
			health effects to workers		
			(long-term occupational		
			exposure); MOE suggests a		
			potential risk of adverse		
			health effects for long-term	1	
			public exposures in the		
			absence of standard risk		
			management measures		
			IMAP- low/high concern		
12	Limonene	138-86-3	Terpene hydrocarbon	Represent important class of terpene solvents	
			(HF chemical)	Replacement of xylene- and toluene- based solvents	
			NCA – not assessed	Soluble and biodegradable	
			IMAP – could not assess	Some data available	
13	Acrylamide polymer	9003-05-8	Anionic polymer	Represent important group of polymers used in hydraulic fracturing	
			(HF chemical)	Being anionic likely to be mobile in geologic formations	
			NCA (hazard screening):	Significant literature available due to possibility of acrylamide impurity (carcinogenicity	
			Low concern for human	controversy)	
			health and environment		

2.3.2.3. Boron

Boron is naturally present in Australian coal seams as a geogenic constituent (Apte et al. 2017b; Ransley et al. 2015). It may also be introduced into the coal seam during hydraulic fracturing as boron compounds are commonly used constituents of hydraulic fracturing fluids (e.g. as a gel cross-linker) (Campin 2015). At pH ranges typical of groundwater systems boron is present as a mixture of the negatively charged borate anion $B(OH)_4^-$ and also a neutral species: $B(OH)_3$ (WHO 1998a). Neither species are known to have a strong sorptive affinity to solid phases. Boron concentrations in groundwater depend on local geology and can typically vary from 0.3 to 100 mg/L (WHO 1998a). Campin (2015) reports boron concentrations in flowback water from coal seams in the Surat range from 0.05 to 56 mg/L (median value of 18 mg/L). Background boron concentrations in key aquifers of the Surat Basin are reported by Ransley et al. (2015) and summarised in Table 2-7. The ANZECC and ARMCANZ (2000) water quality guideline for ecosystem protection for boron in surface waters is 370 µg/L (95% protection level). Subsequent European analysis (Schoderbroeck et al. 2011) yielded a guideline value of 180 µg/L (95% protection level). A recent revision of this value increased it to 830 µg/L (Binet et al. 2016). For the protection of human health, the concentration of boron in drinking water should not exceed 4 mg/L (NHMRC and NHMMC (2011).

Formation	Number of samples	Range	Median
Condamine alluvium	18	0.05-0.3	0.1
Gubberamunda Sandstone	667	0.05-6	0.1
Springbok Sandstone	148	0.01-4	0.3
Walloon Coal Measures	645	0.05-1.7	0.56
Hutton Sandstone-Marburg Subgroup	211	0.02-1.02	0.05

Table 2-7. Background boron concentrations (mg/L) in Surat Basin formations (Ransley et al. 2015).

2.3.2.4. Arsenic

Dissolved arsenic is present in two oxidation states of arsenic in natural waters: As(V) and As(III) (US EPA 2004b). Arsenate is the thermodynamically stable form of arsenic in oxygenated waters (Figure 2-14), however, significant concentrations of As(III) may be found in such waters owing to the slow kinetics of oxidation of As(III) to As(V) (US EPA 2004b). Arsenic(III) may be the major dissolved arsenic species in deep groundwater systems because of the expected redox potential and low oxygen concentrations (Figure 2-14, US EPA 2004b). The sorption of both As(III) and As(V) onto iron hydroxide solid phases is significant and varies with pH (Dixit and Hering 2003) and redox potential (Mallants et al. 2001). Over the pH range 7 to 8, As(III) has a slightly higher affinity for hydrous iron oxide and goethite than As(V) resulting in solid-liquid partition coefficient, K_d , values between a factor of 2 to 2.5 time higher for As(III) than As(V) (Dixit and Hering 2003). Under reducing conditions, the reduction of Fe(III)-oxides to Fe(II) makes the sediment less effective in adsorption of As, while A(III) appears as uncharged As(OH)₃ which has a lower affinity for sorption than As(V) which appears as monocharged H₂AsO₄⁻ (Mallants et al. 2001).

The ANZECC/ARMCANZ (2000) water quality guideline for ecosystem protection for As(V) and As(III) in fresh waters are 13 µg/L and 24 µg/L respectively (both 95% protection level). Over the last 20 years there has been an increasing international focus understanding the mobility and behaviour of arsenic in groundwater systems because of its occurrence at high concentrations in drinking water supplies sourced from shallow aquifers in countries such as Bangladesh (Smedley and Kinniburgh 2002). Arsenic in drinking water is a problem because of its high toxicity and carcinogenicity (Hughes et al. 2011). Based on a global data set, the typical arsenic concentrations in groundwater was found to be less than 10 µg/L,

however groundwater concentrations up to 5000 µg/L may occur in contaminated regions (Smedley and Kinniburgh 2002). Background arsenic concentrations in key aquifers of the Surat Basin are reported by Ransley et al. (2015) and summarised in Table 2-8. Reported values for arsenic(III) in the Precipice Sandstone aquifer at Reedy Creek and Condabri (Surat Basin) are 0.0012 and 0.0005 mg/l, respectively (Prommer et al. 2016).

Formation	Number of samples	Range	Median
Condamine alluvium	18	0.0005-0.01	0.003
Gubberamunda Sandstone	81	0.0005-0.003	0.001
Springbok Sandstone)	Nd	nd	nd
Walloon Coal Measures	148	0.0003-0.022	0.001
Hutton Sandstone-Marburg Subgroup	145	0.0005-0.0031	0.001

Table 2-8. Background arsenic concentrations (mg/L) in Surat Basin formations (Ransley et al. 2015).



Figure 2-14. Eh-pH stability diagram for the dominant arsenic aqueous species at 25°C, total dissolved arsenic concentration: 10⁻⁶ mol/L (US EPA 2004b).

2.3.2.5. Uranium

Uranium (U) has sixteen isotopes; all are radioactive. Several isotopes of uranium are naturally occurring radionuclides, including ²³⁸U (half-life 4.47×10^9 years), ²³⁵U (half-life 7.04×10^8 years), and ²³⁴U (half-life 2.46×10^5 years). Naturally occurring uranium typically contains 99.274 % ²³⁸U, 0.720 % ²³⁵U, and 0.0057 % ²³⁴U by weight (IAEA, 2001). Uranium can exist in the +3, +4, +5, and +6 oxidation states, of which the +4 and +6 states are the most common states found in the environment (Ochs et al. 2015).

Uranium is a geogenic constituent found naturally both in coal seams and geological formations (Apte et al. 2017a). The highest concentrations of uranium are found in igneous rocks such as granite (Taylor 1964). The solution speciation of uranium in natural waters is dominated by two oxidation states: U(VI) and U(IV). U(VI) is more soluble and hence more mobile than U(IV). Most studies have focussed on the U(VI) oxidation state as it is assumed this oxidation state is predominant in groundwater (US EPA 1999a). The solution speciation of uranium is complex (Figure 2-15) with complexation of U(VI) by carbonate (affected by carbonate concentration and pH) and natural organic matter being significant factors influencing the solubility and mobility of uranium (US EPA 1999a). Exposure of U(IV) containing rocks to oxygenated groundwater leads to the oxidation and mobilisation of uranium as U(VI) carbonate complexes (Langmuir 1978). The ANZECC/ARMCANZ (2000) water quality guideline for ecosystem protection (low reliability) for uranium in surface waters is 0.5 μ g/L. Shaw (2010) reported ²³⁸U concentrations in raw produced Australian CSG water up to 1.45 μ g/L.



Figure 2-15. Calculated distribution of U(VI) aqueous species as a function of pH for typical river water (US EPA 1999b) [The species distribution is based on a concentration of 1,000 μg/L total dissolved U(VI)].

2.3.2.6. HMX

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is a widely used nitroaromatic high melting explosive and has applications, along with other explosives, during the hydraulic fracturing process to perforate the well casing prior to allow flow of groundwater and gas into the well and to inject hydraulic fracturing fluids (Savostianov 1991). Unreacted explosives (duds or detonation residues) could end up in the coal seam waters from where could become available for dissolution and subsequent migration. Lewis et al. (2009) discusses several ways why explosives fail to detonate. Most reports of HMX in the environment relate to its discharge from HMX manufacture (TOXNET). The sorption of nitro-containing explosives, including the chemically related TNT and RDX, increases as clay content increases, although HMX still has a relatively low affinity for sorption, even in the case of clay enrichment (Sharma et al. 2013). HMX is therefore considered to be relatively mobile within soil environments (TOXNET). HMX is also relatively stable under and resistant to degradation a range of environmental conditions (aerobic and anaerobic) (Walker and Kaplan 1992, Brannon et al. 2005) and has been detected in groundwater near munitions manufacturing facilities (Lewin et al. 1997).

2.3.2.7. 2-Butoxyethanol

2-Butoxyethanol or 2BE is a surfactant used as pre-flush hydraulic fracturing additive and acid additive. Large quantities have been used in the US and Canada (US Congress Report 2011; Wylde and O'Neil 2011). It is also one of the hydraulic fracturing chemicals used in Australian coal seam gas operations (APPEA 2014). The role of the pre-flush additive is to preferentially wet the formation to allow for better propagation of the fracture through the production zone and post-fracture production of the load water, and ultimately, hydrocarbons (Wylde and O'Neil 2011). Despite being readily degradable, 2BE is also known to bioaccumulate and is generally toxic (Harris et al. 1998). 2BE was declared a Priority Existing Chemical under Australia's National Industrial Chemicals Notification and Assessment Scheme. The assessment of 2BE demonstrated it is highly mobile in soil and water and has been detected in groundwaters underlying municipal landfills and hazardous waste sites in the US.

2.3.2.8. Bronopol

Bronopol is a biocide used in hydraulic fracturing wells in the US (US Congress Report 2011; Kahrilas et al. 2014) and Australia (QGC 2012). Bronopol is also used as preservative in cosmetic products, liquid soaps, and cleaning agents (Madsen et al. 2001). It is very toxic to aquatic organisms such as algae and oysters; the observed LC50 is 1.6 mg/L for *Daphnia magna* (Sigma-Aldrich 2014) and 0.77 mg/L for the Eastern Oyster (US EPA 1995b). Substantial spills into surface waters or streams may therefore have noticeable ecotoxicological effects on aquatic species. Upon degradation in alkaline solutions, bronopol will release formaldehyde, bromide and nitrite (Madsen et al. 2001). Bronopol was shown to produce 2-hydroxymethyl-2-nitropropane-1,3-diol (tris) and 2-bromo-2-nitroethanol (US EPA 1995b). Bronopol has been reported to hydrolyze within 3 h at 60 °C and pH 8, producing formaldehyde, nitrosamines, and other molecules (Swenberg et al. 1980; Dunnett and Telling 1984; Challis and Yousaf 1990; Loeppky 1994; US EPA 1995b). Although, the parent compound (bronopol) is rather short-lived in the environment, its degradation products are toxic (e.g. formaldehyde) and more persistent (e.g. bromonitromethane) (Douglass et al. 1978; Swenberg et al. 1980; Cui et al. 2011).

2.3.2.9. Methyl-chloro-isothiazolinone

Methyl-chloro-isothiazolinone (5-chloro-2-methyl-4-isothiazolin-3-one), also known as MCI, belongs to the thiazole class of biocides and is used as a microbial inhibitor during hydraulic fracturing (APPEA 2014), along with wider antimicrobial applications, such as in personal care products. MCI has a very high water solubility, a high degree of mobility in the environment and is reasonably stable. However, MCI is prone to chemical hydrolysis under alkaline conditions (US EPA

1998b). However, we could not find any measured sorption data on this compound. Toxicity of MCI to aquatic organisms, especially bacteria, is relatively high (Carbajo et al. 2015).

2.3.2.10. Barium

Barium is naturally present in coals seams as a geogenic constituent (Apte et al. 2017a; Ransley et al. 2015). It may also be introduced into the coal seams during drilling as barium sulfate (CAS 7727-43-7) which is used extensively in drilling fluids to increase fluid density (Campin 2015; NSW Chief Scientist and Engineer 2012). Campin (2015) reports barium concentrations in Australian CSG flowback water from 0.049 to 16 mg/L (median value 5.9 mg/L). The mean dissolved barium concentration of produced waters from the Powder River Basin coal bed methane area was 670 μg/L (Rice et al. 2000). Under typical groundwater conditions there are no redox reactions of significance, therefore barium will be present as Ba(II) (WHO 1990). Barium forms an insoluble precipitate with sulfate and when high enough, the ambient concentration of sulfate can control barium concentrations. Sorption onto solids phases is likely to be dominated by electrostatic interactions. Ionic strength, pH, cation exchange capacity and the surface area of the sorbing phases are likely to be controlling factors influencing adsorptive affinity (WHO 1990). The barium guideline value for drinking water is 2 mg/L (NHMRC and NRMMC 2011). The mean crustal abundance of barium is 425 mg/kg (Taylor 1964), however the element is enriched in coal and is present at concentrations up to 3000 mg/kg (Bowen 1966). Typical barium concentrations in surface waters are quite variable and typically range between 7 to 15,000 μ g/L (WHO 1990). In key aquifers of the Surat Basin background barium concentrations are reported by Ransley et al. (2015) and summarised in Table 2-9. Reported values for barium in the Precipice Sandstone aquifer at Reedy Creek and Condabri (Surat Basin) are 0.028 and 2.15 mg/l, respectively (Prommer et al. 2016).

Formation	Number of samples	Range	Median
Condamine alluvium	2	0.151 - 0.4	0.3
Gubberamunda Sandstone	n.d.	n.d.	n.d.
Springbok Sandstone)	n.d.	n.d.	n.d.
Walloon Coal Measures	634	0.016 - 5.3	0.6
Hutton Sandstone-Marburg Subgroup	n.d.	n.d.	n.d.

Table 2-9. Background barium concentrations (mg/L) in Surat Basin formations (Ransley et al. 2015). n.d. = no data

2.3.2.11. Limonene

Limonene occurs naturally in certain trees and bushes, orange peels and pine sap. Limonene and other so-called monoterpenes (terpene hydrocarbons) are released in large amounts mainly to the atmosphere, from both biogenic and anthropogenic sources. Limonene is used as a flavour and fragrance additive in food, household cleaning products, and perfumes. Limonene is also used as a solvent in degreasing metals prior to industrial painting, for cleaning in the electronic and printing industries, and in paint as a solvent. Terpenes such as limonene are replacements for xylene- and toluene-based solvents. Compared with aromatic solvents, terpenes have good solvency, and are biodegradable, less toxic, and less flammable. Limonene is a chemical additive of water and guar based hydraulic fracturing fluid systems; its use has been reported for the US (US Congress Report 2011) and Australia (Santos 2013).

2.3.2.12. Acrylamide polymer

Polyacrylamide is polymeric material used as friction reducer and scale inhibitor within fracturing fluids in Australia (Commonwealth of Australia, 2014b) but is also widely used as a flocculant in water treatment, as a soil conditioner in agriculture and for oil recovery applications (US EPA 1995a, Caulfield et al. 2002). The degree of acrylic acid residues within the polymer leads to polyacrylamide generally being of an anionic nature (Caulfield et al. 2002). It has a very high water solubility, is reasonably resistant to degradation in the environment and are generally of low environmental concern (Caulfield et al. 2002). There is concern, however, relating to the presence of the relatively toxic acrylamide monomer as an impurity or degradation product of the polymer (US EPA 1995a). Depolymerisation of polyacrylamide or hydrolysis of the polymer leads to it having an anionic nature due to the presence of acrylic acid and this, along with its high water solubility, mean that polyacrylamide is expected to be highly mobile in a soil environment (Caulfield et al. 2002).

2.4. Identification of assets within the Gunnedah Basin

Potential assets for use in the spatial analysis and particle tracking analysis are based on the asset registers developed within the Bioregional Assessment Program (O'Grady et al. 2015). For the Namoi subregion, the three asset groups (ecological, economic and socio-cultural assets) and their subgroups and classes are summarised in Table 2-10. Only a subset of the complete asset register was used in the current spatial analysis. The subset was defined on the basis of a buffer zone of approximately 30 km around the study area; this buffer zone was previously defined by CDM Smith (2014) to select water bores in the immediate vicinity of the potentially impacted area. The same buffer zone was used here to focus the spatial analysis on those assets closest to the potentially impacted area. To verify this area was large enough and would encompass all possible groundwater pathways, preliminary particle tracking analysis was undertaken which confirmed that solute particles released at the boundary of the study area would not travel beyond the buffer zone (for details see section 2.6.4.3.1). Particle tracking also indicated contaminants were unlikely to move south from any CSG well (Figure 2-54), therefore spatial analyses of frequency-proximity focused on the area from due west (270°) to due east (90°) of CSG wells (explained in section 3.1).

2.4.1. Ecological assets

The ecological assets group has three subgroups: subsurface features (groundwater), surface water features, and vegetation (Table 2-10). Groundwater features include (Figure 2-16):

• 33 groundwater-dependent assets (groundwater flow systems (aquifers) and groundwater management zones (alluvium or stratum)) and 8 non-water-dependent assets (geological features, i.e. eight geological formations).

Surface water features account for 1142 groundwater-dependent assets, including (Figure 2-17):

- Rivers or stream reaches, tributaries, anabranches or bends,
- Lakes, reservoirs, lagoons or estuaries,
- Waterholes, pools, rock pools or billabongs,
- Wetlands, wetland complexes or swamps,
- Groundwater fed springs (marsh, sedgeland, bog, spring or soak), and
- Floodplains.

The vegetation subgroup has two classes:

- groundwater dependent ecosystems, of which 442 are water-dependent and 246 are non-water-dependent
- habitats of iconic species (67 are water-dependent).

It is important to emphasise that Bioregional Assessments consider the potential impact to the habitat of species, not the individual species per se. All assets in the 'Surface water feature' and 'Groundwater feature (subsurface)' classes of the asset database were assumed to be water-dependent assets and attributed as 'likely'. Assets listed as 'likely' are those with a clear and demonstrated link to aquatic ecosystems, (e.g. aquatic species) (O'Grady et al. 2015). In the current spatial analysis only the water-dependent assets that occur within the 30 km buffer zone⁸ and are located between 270° and 90° north from CSG wells are taken into account.

As can be observed from Figure 2-17 and Figure 2-18, many of the surface water features are either line elements or large polygons. In the spatial analysis, these multipart features have been converted to many single part features to allow calculation of distance between CSG wells and geographically separate parts of elements (see further section 3.1).

⁸ This buffer zone was previously defined by CDM Smith (2014) to select water bores in the immediate vicinity of the potentially impacted area of the study area

Table 2-10 Summary of ecological assets within the preliminary assessment extent of the Namoi subregion (O'Grady et al. 2015). Only the water-dependent assets within the 30-km buffer area are considered in the current study.

Subgroup	Class	Not in water- dependent asset register	In water- dependent asset register	Total assets (asset list)	Assets within 30 km buffer between 270° and 90° from CSG wells
Groundwater feature (subsurface)	Aquifer, geological feature, alluvium or stratum	8	33	41	10
	Groundwater total	8	33	41	10
Surface water feature	River or stream reach, tributary, anabranch or bend	0	767	767	109
	Lake, reservoir, lagoon or estuary	0	31	31	6
	Waterhole, pool, rock pool or billabong	0	10	10	0
	Wetland, wetland complex or swamp	0	279	279	105
	Marsh, sedgeland, bog, spring or soak	0	21	21	1
	Floodplain	0	34	34	8
	Surface water total	0	1142	1142	229
Vegetation	Groundwater- dependent ecosystem	246	442	688	43
	Habitat (potential species distribution)	26	67	93	19
	Vegetation total	272	509	781	62
Total		280	1684	1964	301





- Aquifer, geological feature, alluvium or stratum Project Area 30km Buffer
- River
- Proposed CSG Well
- Town



Figure 2-16 Ecological assets subgroup "groundwater feature/subsurface" within the Gunnedah basin subregion. 30 km buffer area based on groundwater impact assessments from projected CSG extraction. Labels are linked to large polygons.



River or stream reach, tributary, anabranch or bend

Wetland, wetland complex or swamp

Catchment



Figure 2-17 Ecological assets subgroup "surface water feature" within the Gunnedah basin subregion. 30 km buffer area based on groundwater impact assessments from projected CSG extraction. Floodplain polygon is a multipart feature that was split into individual features for spatial analysis.



Ecological Assets (Vegetation Subgroup)

- Habitat (potential species distribution)
- Groundwater-dependent ecosystem
- Project Area 30km Buffer
- Proposed CSG Well
- Town



Figure 2-18 Ecological assets subgroup "Vegetation" within the Gunnedah basin subregion. 30 km buffer area based on groundwater impact assessments from projected CSG extraction. Groundwater dependent ecosystem polygon is a multipart feature that was split into individual features for spatial analysis.

2.4.2. Economic assets

Economic assets for the Namoi subregion are divided into groundwater and surface management zones (Table 2-11). The groundwater management zones subgroup has four classes (for details, see O'Grady et al. 2015):

- Groundwater features used for water supply (currently zero elements),
- Water supply and monitoring structure (currently zero elements),
- Water access right: has 1936 elements (groundwater bores). Each water access right licence can have one or multiple works associated with it, where the works is the location where the water is extracted through a bore or pump,
- Basic water right (stock and domestic): the right of those adjacent to aquifers underlying the land to extract water for domestic and stock use without a water access licence. A total of 7017 elements are included in the database (groundwater bores).

For the entire Namoi subbioregion, the median bore depth is 36 m, with a maximum of 1200 m, so most water bores tap shallow alluvial groundwater systems (less than 150 m) (O'Grady et al. 2015). An analysis of water bores located within the 30 km buffer area of the study area indicated groundwater abstraction in close proximity to the study area is limited by land use constraints within the Pilliga Forest and smaller groundwater yields.

Figure 2-19 shows registered bores in the vicinity of the study area. Within the National Groundwater Information System (BOM) for NSW there are a total of 141,297 bore records. Within 30km of the proposed CSG wells in the Namoi subregion (and records filtered where drilled/bore depth was zero or NULL), there were a total of 3,318 bore records. The majority of these bores (96%) have a depth <150m and most of the bores deeper than 150 m are likely to be screened within the Pilliga Sandstone, which is typically 150 to 300 m thick in the Project area. Bores 150-300 m deep and identified as being within the Gunnedah Basin GMA to the south and southeast of the Project area, are possibly screened within the Garrawilla Volcanics (CDM Smith 2014).

The targets for coal seam gas extraction are the coal seams of the Maules Creek Formation (primary targets) and the Hoskissons Coal in the Black Jack Group (secondary targets). A GIS analysis of bore records intersecting the Maules and Hoskinssons formations was conducted. Maules and Hoskinssons formations were isolated from the Namoi groundwater model grid layers. Bore records (from the NGIS) were extracted from within the groundwater model area and filtered where drilled/bore depth was zero or NULL. Bore elevations (mAHD) were calculated by substracting the bore/drilled depth (m) from the reference (land) elevation (mAHD). No information on open/screened section depths were contained within the NGIS; an assumption was made that the bores were open at the maximum bore/drilled depth. Bore records were then queried for those intersecting (on x, y and z coordinates) with the Maules and Hoskinssons formation groundwater model grid layers.

No bore records intersected the Maules Creek Formation. A total of 28 bore records (with status of either 'functional' or 'unknown') intersected the Hoskissons Coal layer. Uses of these bores included: household water supply for household needs e.g. washing, toilet; community water supply; water supply for livestock; and water supply for irrigated agriculture. All 28 bores were located south of the Project area and proposed CSG wells and according to the particle tracking analysis were unlikely to be in the path of any contaminants release from the CSG wells.







Figure 2-19 Licensed groundwater bores less than (left) and greater than (right) 150 m deep (modified from CDM Smith 2014). The black cross-hatching shows licensed bores with unspecified groundwater management area (GMA). Red polygon is the study area (encloses the proposed CSG wells as shown in Figure 2-16 through 2-18).

The surface water management subgroup has the following classes (for details, see O'Grady et al. 2015):

- Surface water feature used for water supply (currently zero elements),
- Water supply and monitoring infrastructure (currently zero elements),
- Water access right (this requires a licence both for the works and the extraction of the water). The extraction of the water can be for a range of purposes including irrigation, commercial, industrial, farming, dewatering, mining, intensive agriculture etc.,
- Basic water right (stock and domestic): the right of those adjacent to rivers, estuaries, or lakes extract water for domestic and stock use without a water access licence.

Occurrence of further economic assets have been depicted in Figure 2-20 and Figure 2-21.

Table 2-11 Classification of economic elements to create economic assets in the Namoi asset database (O'Grady et al. 2015). Only the water-dependent assets within the 30-km buffer area are considered in the current study.

Subgroup	Class	Total number of elements	Number of elements within 30 km buffer between 270° and 90° from CSG wells
Groundwater management zone or area (surface area)	A groundwater feature used for water supply	0	0
	Water supply and monitoring infrastructure	0	0
	Water access right	1,937	288
	Basic water right (Stock and domestic)	7,044	1,196
	Groundwater total	8,981	1,484
Surface water management zone or area (surface area)	A surface water feature used for water supply	0	0
	Water supply and monitoring infrastructure	0	0
	Water access right	1,459	134
	Basic water right (stock and domestic)	57	17
	Surface water total	1,516	151
Total		10,497	1,635



Economic Assets (Groundwater management Subgroup)

Management Zones

- Groundwater management zone (water access right)
- Groundwater management zone (stock and domestic)

Groundwater Bores

- Basic water right (stock and domestic)
- Water access right



Namoi River
Proposed CSG Well

Town





Figure 2-20 Economic Assets subgroup "Groundwater Management Zone or Area" within the Gunnedah basin subregion. 30 km buffer area based on groundwater impact assessments from projected CSG extraction. Assets include groundwater bores for purposes including water conservation, domestic, stock, teaching and 'unknown'; and Groundwater Management Plan areas for the Upper and Lower Namoi sources, NSW GAB, and the NSW MDB Fractured and NSW MDB Porous Rock sources.



Economic Assets (Surface water management Subgroup)



Figure 2-21 Economic Assets subgroup "Surface Water Management Zone or Area" within the Gunnedah basin subregion. 30 km buffer area based on groundwater impact assessments from projected CSG extraction. Assets include Water Sharing Plan areas (management zones) for Basic Water Rights (stock and domestic) and Water Access Right locations for the Lower Namoi River and the Bohena, Brigalow, Bundock, Eulah, Spring, Bobbiwaa, Maules, Pian and Millie Creeks.

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2.4.3. Sociocultural assets

A total of thirty-one heritage and ten Indigenous assets were included in the asset database. 22 out of the 31 heritage assets are considered water dependent. This includes 14 assets that are located within the maximum flood extent and eight assets that are assumed to contain water-dependent features (O'Grady et al. 2015). Eight out of ten of the Indigenous assets are considered to be water dependent based on the presence of floodplain and wetland areas within their spatial extent. Sociocultural assets within the 30 km study area buffer area are shown in Figure 2-22. These include 8 heritage sites and 1 indigenous site, however, the Pilliga Nature Reserve is outside the 270° to 90° directional range from the proposed CSG wells and was excluded from the frequency-proximity analysis.



Figure 2-22 Sociocultural assets within the Gunnedah basin subregion. 30 km buffer area based on groundwater impact assessments from projected CSG extraction.

2.5. Identification of assets within the Surat Basin

A summary of the registered and not registered water dependent assets and assets located within the buffer area defined by the extent of particle tracking distances for the Maranoa-Balonne-Condamine (MBC) subregion is given in Table 2-12, Table 2-13, and Table 2-14. This includes ecological, economic and sociocultural asset groups (Mitchell et al. 2015).

Note that for the spatial proximity analysis on the Surat Basin study site, the buffer area (the maximum search distance) was larger than the 30 km buffer around CSG wells due to particles moving beyond the 30 km buffer (see Section 2.6.5). The buffer area was defined as the maximum extent of the particle pathways. This differed from the buffer area applied to the Gunnedah Basin study area analysis where particle movement remained within 30 km of CSG wells (see Section 2.6.4).

2.5.1. Ecological assets

Numerous ecological assets were located within the 30 km buffer including aquifer, geological feature, alluvium or stratum (10 assets), river or stream reach, tributary, anabranch or bend (109 assets), groundwater-dependent ecosystem (54 assets), and habitat (potential species distribution) (49 assets) (Table 2-12).

Table 2-12 Summary of ecological assets within the preliminary assessment extent of the MBC subregion. Only the water-dependent assets within the particle tracking extent buffer area are considered in the current study. Note that not all assets may be visible on the graphical displays due to clustering of data points.

Subgroup	Class	Not in water- dependent asset register	In water- dependent asset register	Total assets (asset list)	Assets within the particle tracking extent buffer between 180°S and 90°E from CSG wells
Groundwater feature (subsurface)	Aquifer, geological feature, alluvium or stratum	3	23	26	10
Surface water feature	Floodplain	0	6	6	0
Surface water feature	Lake, reservoir, lagoon or estuary	0	55	55	1
Surface water feature	Marsh, sedgeland, bog, spring or soak	0	267	267	9
Surface water feature	River or stream reach, tributary, anabranch or bend	39	695	734	106
Surface water feature	Waterhole, pool, rockpool or billabong	1	554	555	6
Surface water feature	Wetland, wetland complex or swamp	0	111	111	15
Vegetation	Groundwater-dependent ecosystem	35	313	348	54
Vegetation	Habitat (potential species distribution)	119	171	290	49
Vegetation	Riparian vegetation	0	20	20	5



- 11539, Precipice Sandstone
- 11568, Springbrok Sandstone
- 11583, Walloon Coal Measures 11586, Wandoan Formation



Figure 2-23 Ecological assets Groundwater Feature (subsurface) Subgroup, Aquifer, geological Feature Class within the Surat Basin study area. Numbers refer to polygons depicting aquifers or geological features.



Figure 2-24 Ecological assets Surface Water Feature Subgroup within the Surat Basin study area. Not all assets of the "Marsh, sedgeland, bog, spring or soak" subgroup are visible due to clustering of data points.



Ecological Assets - Vegetation Subgroup GDEs and Riparian Vegetation



Figure 2-25 Ecological assets Vegetation Subgroup within the Surat Basin study area.

2.5.2. Economic assets

Economic assets within the 30 km buffer included groundwater management zone or area (surface area) subgroup (basic water right (stock and domestic) and water access right classes) (22 assets), and surface water management zone or area (surface area) subgroup (Water access right class) (7 assets) (Table 2-13).

Table 2-13 Summary of economic assets within the preliminary assessment extent of the MBC subregion. Only the water-dependent assets within the particle tracking extent buffer area are considered in the current study.

Subgroup	Class	Not in water-	In water-	Total assets	Assets within
		dependent	dependent	(asset list)	the particle
		asset register	asset		tracking
			register		extent buffer
					between
					180°S and
					90°E from
					CSG wells
Groundwater management	Basic water right	0	38	38	14*
zone or area (surface area)	(stock and domestic)				
Groundwater management	Water access right	0	76	76	8**
zone or area (surface area)					
Groundwater management	Water supply and	0	13	13	0
zone or area (surface area)	monitoring				
	infrastructure				
Surface water management	Basic water right	0	32	32	0
zone or area (surface area)	(stock and domestic)				
Surface water management	Water access right	0	145	145	7
zone or area (surface area)					
Surface water management	Water supply and	0	6	6	0
zone or area (surface area)	monitoring				
	infrastructure				

* Assets with multipoint features (1652 in total)

** Assets with multipoint features (390 in total)



Economic assets Groundwater management zone subgroup



Figure 2-26 Economic assets Groundwater management zone Subgroup within the Surat Basin study area.



Economic assets Surface water management zone subgroup



Figure 2-27 Economic assets Surface water management zone Subgroup within the Surat Basin study area. Water access right includes groundwater and surface water management area.

2.5.3. Sociocultural assets

Sociocultural assets within the particle tracking extent buffer included 1 heritage site and 1 recreation area (Table 2-14).

Table 2-14 Summary of sociocultural assets within the preliminary assessment extent of the MBC subregion. Only the water-dependent assets within t	he
particle tracking extent buffer area are considered in the current study.	

Subgroup	Class	Not in water- dependent asset register	In water- dependent asset register	Total	Assets within the particle tracking extent buffer between 180°S and 90°E from CSG wells
Cultural	Heritage site	34	50	84	1
Cultural	Indigenous site	7	59	66	0
Social	Recreation area	7	26	33	1



Figure 2-28 Sociocultural assets within the Surat Basin study area.

2.6. **Conceptualisation of fate and transport pathways**

2.6.1. Introduction

Within a risk assessment paradigm, conceptual model(s) could strongly inform the identification of hazards and could be used to help select appropriate scenarios for further hazard, exposure, consequence, likelihood, and / or risk assessment. The phasing of CSG operations and the mitigating measures industry have put in place directly informs this conceptualisation. For example, the lifetime of an individual CSG well or an entire CSG well field can be divided into different phases of operation (Figure 2-29; Mallants et al. 2017a). Each phase has a number of typical activities with a relatively well-defined duration and set of risks. Importantly, these risks are not equally distributed across time and space.

Based on the three major phases in the life-cycle of a CSG well field that potentially provide the largest risk to groundwater contamination (Figure 2-29), i.e. the "pressurisation" phase, the "depressurisation" phase, and the "return to equilibrium" phase, three conceptual models can be envisaged from which chemical release scenarios can be constructed. Conceptualisations for shallow groundwater for the first two phases have been reported in Mallants et al. (2017a). Regarding deep groundwater, there are other sources and pathways that need consideration. These are discussed on the basis of Figure 2-30.



Figure 2-29 Phases of development and operation of a CSG project (Mallants et al. 2017a).

During the pressurisation or injection phase, leakage of hydraulic fracturing fluids can occur via fracture growth into an aquifer (Pathway A in Figure 2-30), via fracture growth into a well located in the same coal seam formation (Pathway B in Figure 2-30), via a poor-integrity well casing (Pathway C in Figure 2-30; US EPA 2012a), or via faults or fractured zones connected to the coal seams being hydraulically fractured (Pathway D in Figure 2-30). A detailed discussion of these potential pathways is provided in Section 2.6.2.

Because groundwater flow direction is towards the coal seam formation and its production wells during the "depressurisation" phase, and also during most of the "return to equilibrium" phase (Wu et al. 2016), leakage to overlying or underlying aquifers of the residual fraction of hydraulic fracturing fluids remaining in the coal seam formations is likely very limited. One potential pathway during the "depressurisation" phase is for coal seam water containing residues of the hydraulic fracturing fluid and geogenics to leak into beneficial aquifers via an existing and productive water bore screened in the coal seam aquifer (Pathway B in Figure 2-30). The depressurisation and associated water flow caused by the groundwater bore can be stronger than that caused by the CSG wells, especially in the beginning of the depressurisation phase. As a result, the water bore can become a sink for hydraulic fracturing fluids. In practice, however, water bores in the vicinity of CSG wells that could cause such pathway would be plugged to stop any flow of water and/or gas.

The "return to equilibrium" phase may take up to several hundred years, in some cases even more than 1000 years (Mallants et al. 2017b; Wu et al. 2016), and is characterised by a very slow re-pressurisation of the coal seam formation, but with an overall flow direction still towards the coal seams until some new equilibrium has been established. Where
groundwater abstraction occurs, either within the coal seams or above, flow may locally be oriented towards the groundwater well (i.e. outside the gradually shrinking cone of depression created during the depressurisation) which could accelerate transport of contaminants towards the well through previously created pathways (e.g. fractures). Clearly, these pathways might intersect or overlap. However, to usefully inform assessments of pathway features in terms of travel time and attenuation, a relatively small and manageable number of emission scenarios has been developed. These scenarios have also been informed by the national and international literature review (Section 2.1):

- wellbore integrity failure during injection (well rupture), production (wellbore failure), or decommissioning/abandonment (well integrity failure) providing a well pathway,
- an offset, proximal extraction well pathway,
- fracture growth into an overlying aquifer generating an induced fracture pathway,
- loss of hydraulic fracturing fluid via faults.

Having defined the release and migration pathways from the coal seam formation into adjacent formations, the migration paths to receptors also need to be more carefully conceptualised. Typical receptors include groundwater abstraction wells location within or above / below coal seam formations, groundwater aquifers connected to coal seam formations via faults, surface water features such as springs, groundwater dependent vegetation, groundwater fauna, wetlands and stream receiving deep groundwater (further details in section 2.6.2).



Figure 2-30 Conceptualisation of possible contaminant pathways linked to deep groundwater and receptors at the CSG site for injection phase. Conceptualisations of pathways to shallow groundwater were developed in the National Assessment of CSG Chemicals Project (Mallants et al. 2017a).

The conceptual models developed throughout this study include the following elements:

- description of the contaminant source(s) relevant to deeper groundwater, including below-ground chemical leaks within the target coal formation and leaks in beneficial aquifers
- for each type of chemical, the likely fate and transport pathway of the chemical. Fate of a chemical depends on
 its chemical and physical properties including its persistence, solubility, binding ability, and how it interacts with
 the underground ecology and the (hydro)geological environment in which it is released. Release to groundwater
 may result in movement away from the source over an extended period and distance, depending on
 hydrogeological conditions. Depending on persistence, solubility and geological binding properties, chemicals
 released to groundwater have potential to remain at a site for many years or percolate via preferential flow
 paths towards various receptors. Chemical fate and transport pathways that affect potential exposure routes for
 sensitive receptors will be accounted for.
- hydrogeological conceptualisations of typical Australians CSG basins.
- description of the receptors (groundwater use and groundwater dependent ecosystems, including wetlands, springs, streams).
- statement of underpinning assumptions and hypotheses.

2.6.2. Plausible fate and transport release pathways

Building on the literature review on plausible fate pathways (Section 2.1.1), four plausible fate and transport release scenarios have been developed for which the chemical-specific DAF in groundwater-related receptors will be assessed. The likelihood for each of these scenarios is defined in subsequent Sections 2.6.2.1 to 2.6.2.3. The following scenarios are considered to represent a sufficiently broad range of flow conditions that may provide pathways for chemical transport into aquifers (Figure 2-31):

- Fracture growth into an overlying aquifer (Pathway A): This scenario considers hydraulic fracture fluid loss into an overlying aquifer. The scenario considers site conditions that favour height growth of a vertical hydraulic fracture upward towards and into a shallower aquifer. The volume of fracture fluid lost from the fracture into the aquifer may then be calculated for different injected fracturing fluid types, namely water or crosslinked gel.
- Fracture growth into a well through pre-fracturing permeability and new fractures (Pathway B): This involves two wells within the same coal seam, connected by a pre-existing hydraulic facture; it will be used to illustrate the effect of a CSG injection well on the rate of fluid production from the second groundwater well and the likely chemical concentration in such well.
- Well rupture during injection (Pathway C): This scenario considers rupture of a cased well during a fracturing injection operation. If a cased part of the wellbore that passed through an aquifer were to rupture while a fracturing fluid was being pumped down the casing, the fracturing fluid could escape directly into the aquifer.
- Fracture growth into a fault (Pathway D): assessment of leakage potential via a fault that connects the coal seam to an overlying aquifer.

For each of the above plausible failure scenarios that may lead to contamination of groundwater resources following hydraulic fracturing operations, the study determines i) if these failure scenarios are physically possible, and, ii) if so, under what properties and conditions (flow, geomechanical, hydraulic fracturing operations), as well as iii) the envelope of possible behaviour (see Appendix 7). The determination was based on a review of national and international literature, and will make use of findings from the NCA study (Jeffrey et al. 2017a), and the "Bioregional Assessment Conceptual Modelling" reporting products for the Gloucester, Maranoa-Balonne-Condamine and Namoi subregions and the Bioregional Assessment sub methodology for "Developing the Conceptual Model of Causal Pathways" (Henderson et al. 2015).

Determination of baseline leak-off volume and chemical mass remaining in coal seam will involve a quantitative assessment of the volume and mass of injected HF chemicals, the likely range of chemical concentrations in the coal seam formation pore water for difference assumptions of fluid leak-off⁹, hydraulic fracture properties, and rock properties. These calculations would provide the baseline source characteristics to be considered for evaluation of other scenarios.

In developing pathway conceptualisations, use was made where possible of the IAN-Graphics software. Diagrams were based on Australian CSG well constructions favouring vertical wells. In assessing the fate pathways, both single well releases and multiple-well releases will be considered (e.g. see the particle tracking pathways involving multiple-well releases, Sections 2.6.4.3 and 2.6.5.3). The latter allows an assessment of cumulative effects in terms of total chemical mass load. A base case scenario has been developed for comparison with scenarios/conceptualisations A, C, and D; the base case does not include any preferential flow path, only existing connectivity through interconnected coal seam-aquifer systems (scenario B in Figure 2-31). The base case, including representation of relevant receptors, uses the hydrogeological conceptualisation discussed in Sections 2.6.4.1 and 2.6.5.1.

Four possible pathways have been considered for the analysis. They are considered to cover plausible pathways identified during the literature review, recognising that for each pathway several calculation cases can be developed in which parameters are changed over a reasonable range to produce a range of results rather than a single output. In this way one can better explore under which conditions attenuation is enhanced or reduced, and the results become applicable for a broader range of flow conditions reflecting variations in geology and hydrogeology (e.g. proximity of faults and flow properties, geological attenuation characteristics of aquitards, etc.).



Figure 2-31 Example of plausible fate and transport release pathways. A water bore and wetland are shown as typical receptor.

 $^{^{9}}$ The fluid that is lost during a hydraulic fracture treatment by flow into the surrounding permeable rock

Each plausible release pathway from Figure 2-31 is discussed with reference to current industry practice. Subsequently, the hazard to deeper groundwater is reviewed with reference to six lines of evidence (details about lines of evidence are available in Appendix 7):

- Basic hydraulic fracture growth models to provide bounding data points;
- Industry standard numerical modelling of hydraulic fracture growth;
- Analysis of samples from monitoring / water wells;
- Remote hydraulic fracture growth monitoring;
- Interpretation of injection pressure data; and
- Observation of key environmental receptors.

The lines of evidence 1 and 2 (modelling of hydraulic fracture growth) are underpinned by numerical simulations based on a conceptual geomechanical model that has been constructed from geological information provided by CDM Smith (2014); simulations have been undertaken in relation to plausible Pathways B, C and D (see Appendix 7 for details).

2.6.2.1. Plausible pathway A: fracture growth into an aquifer

In plausible Pathway A, the vertical extent of the hydraulic fracture is such that it connects the CSG production interval to the water bearing aquifer through the overlying aquitard. The vertical and horizontal extent of the hydraulic fracture growth are governed by the injected fracture fluid volume and the leak-off into the formation. While hydraulic fracturing engineers have some control over fracture size through selection of fluid viscosity and injection rate, variations from designed fracture extent may come from inaccurate knowledge of the geology or from screen-out where proppant becomes blocked and halts hydraulic fracture growth.

It is well known that a thick, unfractured aquitard that is highly stressed, strong, and stiff relative to the coal seam, will lead to an extremely small likelihood that the hydraulic fractures will grow out of zone as hydraulic fractures favour growth in lower stress layers, while higher stress layers act as barriers to fracture growth (Bunger 2015). It is also clear that growth out of the zone is likely if the bounding geological layers possess none of the known attributes that comprise a barrier to hydraulic fracture growth.

Maxwell (2011) demonstrated that industry fracture models can be prone to over estimation of height growth compared to the results of microseismic fracture monitoring. Industry fracture models currently also are unable to predict complex fracture geometry such as T-shaped growth as seen in Rodvelt (2014) and Rogers (1994) or three-dimensional forms of multiple fractures (Kear et al. 2013). The disconnect between the modelled fracture growth predations and post-treatment analysis has led to a range of estimates of the likelihood of out of zone hydraulic fracture growth creating a conductive pathway between the production interval and an overlying water bearing aquifer (Broomfield 2012; Fisher and Warpinski 2012; King 2012; Maxwell 2011). Table 2-15 below reviews the applicability of each line of evidence to plausible Pathway A.

If the best well completion practises are followed and the lines of evidence from Table 2-17 and the lack of reported cases are considered, then the risk of hydraulic fracturing contaminants being transported via a fracture growing into an aquifer in plausible Pathway A could be considered exceptionally unlikely (medium confidence) (Mastrandrea et al. 2010) for the purposes of this hazard screening tool. Table 2-15 Lines of evidence relevant to plausible Pathway A.

Line of evidence	Applicability to hazard assessment of Pathway A
1: Basic hydraulic fracture growth and fluid transport models to provide bounding data points	Moderately applicable. Basic hydraulic fracture growth models provide bounding data points for a simplistic estimate of extent of vertical hydraulic fracure growth. The output of basic hydraulic fracture growth models can be compared to the vertical separation of the water bearing aquifer and will provide a useful line of evidence for plausible pathway A.
2: Industry standard numerical modelling of hydraulic fracture growth and fluid transport	Moderately applicable. Industry standard numerical modelling provides a more accurate estimate of the extent of the vertical hydraulic fracture growth. The output of industry standard numerical models can be compared to the vertical separation of the water bearing aquifer and will provide a key line of evidence for plausible Pathway A.
3: Analysis of samples from monitoring / water well	Highly applicable. Contaminants transported to the water bearing aquifer along plausible Pathway A should conceivably be detected in samples from monitoring or water wells.
4: Remote hydraulic fracture growth monitoring	Highly applicable. Remote monitoring of hydraulic fracture growth would provide an estimate of vertical fracture extent to compare to the vertical separation of the water bearing aquifer and to provide a useful line of evidence for plausible Pathway A.
5: Interpretation of injection pressure data	Loosely applicable. Vertical out of seam hydraulic fracture growth may produce an injection pressure plot that is different to hydraulic fracture growth contained in the CSG production interval but it is unlikely that this difference would be able to be accurately identified.
6: Observation of key environmental receptors	Currently no data are available.

2.6.2.2. Plausible pathway B: fracture growth into a well

In plausible Pathway B, a hydraulic fracture grown in a CSG production interval directly intersects a water bore in the same geological interval. When assessing the likelihood of plausible Pathway B, it is important to have a useful estimate of the horizontal extent of the hydraulic fracture.

Obtaining such an estimate is not straightforward as fluid transport and crack propagation behaviour in coal is often badly predicted by linear theories. Additionally, any height growth will also directly reduce the horizontal extent of hydraulic fracture growth. As a result, simple, tractable solutions can give very poor estimates of hydraulic fracture length and therefore must be applied only with caution and in a manner that is cognizant of their limitations. In this case such simple models are used to provide bounding data points for the maximum possible horizontal extent of fracture growth. Based on modelling analysis, it was considered extremely unlikely for horizontal fractures to extend further than approximately 300m (for given fracture treatment parameters).

Table 2-16 Lines of evidence relevant to plausible Pathway B.

Line of evidence	Applicability to hazard assessment of Pathway B
1: Basic hydraulic fracture growth models to provide bounding data points	Highly applicable. Basic hydraulic fracture growth models provide bounding data points for the maximum potential extent of hydraulic fracture growth. Plausible Pathway B involves the intersection of the growing hydraulic fracture and a water bore that draws from the CSG production interval. The maximum potential extent of the hydraulic fracture is relevant when reviewing the proximity of the water bore to the production borehole.
2: Industry standard numerical modelling of hydraulic fracture growth and fluid transport	Highly applicable. Industry standard numerical modelling provides a more accurate estimate of the extent of the hydraulic fracture growth. The output of industry standard numerical models can be compared to the horizontal and vertical location of water bores in relation to the production borehole.
3: Analysis of samples from monitoring / water well	Highly applicable. Contaminants transported to the water bore via plausible Pathway B should conceivably be detected in samples from the water bore.
4: Remote hydraulic fracture growth monitoring	Highly applicable. Remote monitoring of hydraulic fracture growth is especially applicable for assessing this plausible pathway. If the water bore that draws from the CSG production interval is monitored for hydraulic fracture intersection then this would provide direct evidence of the establishment of a plausible transport pathway.
5: Interpretation of injection pressure data	Moderately applicable. An intersection between the growing hydraulic fracture and a water bore may cause an abnormality in the injection pressure plot. However the cause of this abnormality may not be clearly distinguishable from a fracture intersection with a highly permeable zone.
6: Observation of key environmental receptors	Currently no data are available.

2.6.2.1. Plausible pathway C: well rupture during injection

Plausible Pathway C describes a scenario where migration of hydraulic fracturing fluid occurs along the annulus of a poorly completed well. Like hydraulic fracturing, well completion technology has a long history. Best practice begins during the drilling process by ensuring the drilling fluid is appropriately designed so that breakout of the wellbore, which can lead to cementing difficulties, is minimised. Casing and cementing technology is also well-established, and historically wells that leak are often, if not invariably, the product of well construction that is below best practice.

A number of factors can impact on well integrity, including:

- poor drill hole conditions resulting from wellbore breakouts during drilling,
- casing that is not centred in the hole,
- cement that does not perform well under physio-chemical conditions encountered in a given well.

A review of the likelihoods of onshore petroleum well failure in a North American context is presented in King and King (2013). However, Wu et al. (2016) identify that, to date there have not been any estimates made of failure rates for CSG wellbores in Australia.

As a full review of failure rates for CSG wellbores in Australia is beyond the scope of this report; the current hazard risk screening tool will be limited to identification and discussion of applicable lines of evidence in Table 2-17 below (see Appendix 7 for details about the different lines of evidence that must be gathered and reviewed for each of the plausible transport release pathways).

If the best well completion practises are followed and recognising the lack of reported cases, then there is high to very high confidence that the risk of hydraulic fracturing contaminants being transported up the wellbore annulus in plausible Pathway C could be considered unlikely.

Line of evidence	Applicability to hazard assessment of Pathway C
1: Basic hydraulic fracture growth models to provide bounding data points	Highly applicable. While hydraulic fracture growth models are only limited in applicability due to the nature of plausible Pathway C, fluid transport models could assist in determining the propensity of hydraulic fracture fluid to migrate up a poorly sealed cement well annulus.
2: Industry standard numerical modelling of hydraulic fracture growth and fluid transport	Highly applicable. Hydraulic fracture growth models are only limited in applicability due to the nature of plausible Pathway C. Industry standard fluid transport models could provide additional insight into the flow of hydraulic fracture fluid up a poorly sealed cement well annulus and into a highly permeable formation.
3: Analysis of samples from monitoring / water well	Highly applicable. Contaminants in the water bearing aquifer should conceivably be detected in samples from monitoring or water wells.
4: Remote hydraulic fracture growth monitoring	Moderately applicable. Monitoring of hydraulic fracture growth should provide evidence if the hydraulic fracturing stimulation was rendered ineffective by a highly conductive loss of wellbore integrity or if the loss of wellbore integrity was exacerbated by attempted hydraulic fracturing stimulation.
5: Interpretation of injection pressure data	Loosely applicable. Hydraulic fracturing fluid flowing up the annulus of a wellbore should have a different injection pressure response to a normal hydraulic fracture treatment. However the cause of this abnormality may not be clearly identifiable.
6: Observation of key environmental receptors	Currently no data are available.

Table 2-17 Lines of evidence relevant to plausible Pathway C.

2.6.2.2. Plausible Pathway D: fracture growth into a fault

In plausible contaminant transport Pathway D, an unidentified natural fault spanning the water bearing aquifer, the aquitard and the CSG production interval exists either:

• In the path of the growing hydraulic fracture in the CSG production interval, or

• Directly intersects the specific section of the borehole in the CSG production interval, which is isolated and pressurised to grow a hydraulic fracture.

In either scenario, during fracture growth the pre-existing fault is pressurised, reopened and acts as a preferential pathway for the fracture fluid. Hydraulic fracture intersection of natural faults has been suggested as the mechanism that causes larger than expected fracture height growth events in the Barnett and Jonah fields in the USA (Fisher and Warpinski 2012; Warpinski 2009; Wolhart et al. 2006).

Often a "step-rate" or a "step-down" test is conducted at the start of a treatment where injection pressure is recorded for different flow rates. Either of these tests should identify a highly conductive fault that directly intersects the borehole in the CSG production interval by a marked discrepancy in the test results compared to similar wells in the field.

The volume of hydraulic fracture fluid and proppant pumped for the fracture treatment is believed to limit the height growth in the same way as a typical hydraulic fracture (Fisher and Warpinski 2012). Therefore, the likelihood of the fracture extending through the aquitard to the water bearing aquifer is minimal. In fact, logically a highly conductive fault would more likely cause the fluid to preferentially flow downwards due to gravitational effects rather than towards the surface.

During the fracturing treatment, a highly conductive fault either intersecting the borehole or intersecting the growing hydraulic fracture in the CSG production interval would likely cause a corresponding abnormality in the treatment pressure. The hydraulic fracture engineers could identify this abnormality in the treatment pressure and abandon the fracturing operation. If the engineers did not notice the discrepancy, they would pump the planned volume of fracturing fluid and proppant.

A worst case scenario exists where a critically stressed fault could be pressurised and reactivated by a growing hydraulic fracture. In this scenario it is theoretically possible that the conductivity of the fault could be enhanced between the water bearing aquifer and the CSG production interval. The reactivated fault would not retain much permeability as proppant would tend to travel downwards in a highly conductive channel rather than upwards towards the aquifer and the fracture would not continue to grow once it reached the aquifer as all the fluid pressure would be released. It is assumed that such a significant geological structure would be mapped and well understood by the operator prior to conducting any facture treatment and therefore this worst case scenario is excluded from consideration in this report.

Line of evidence	Applicability to hazard assessment of Pathway D
1: Basic hydraulic fracture growth and fluid transport models to provide bounding data points	Highly applicable. Basic hydraulic fracture growth models provide bounding data points for the maximum potential extent of hydraulic fracture growth. Plausible pathway D involves the intersection of the growing hydraulic fracture and a natural fault. The maximum potential extent of the hydraulic fracture is relevant when reviewing the proximity of natural fault systems to the production borehole.
2: Industry standard numerical modelling of hydraulic fracture growth and fluid transport	Highly applicable. Industry standard numerical modelling provides a more accurate estimate of the extent of the hydraulic fracture growth. The output of industry standard numerical models can be compared to the horizontal and vertical location of natural faults in relation to the production borehole.
3: Analysis of samples from monitoring / water well	Highly applicable. Contaminants transported to the water bearing aquifer along plausible pathway should conceivably be detected in samples from monitoring or water wells.

Table 2-18 Lines of evidence relevant to plausible Pathway D.

4: Remote hydraulic fracture growth monitoring	Highly applicable. Tilt-meter or micro-seismic monitoring of hydraulic fracture growth would likely identify growth into or re-activation of a significant natural feature.
5: Interpretation of injection pressure data	Moderately applicable. An intersection between the growing hydraulic fracture and a natural fault may cause an abnormality in the injection pressure plot. However the cause of this abnormality may not be clearly distinguishable from a fracture intersection with another highly permeable zone.
6: Observation of key environmental receptors	Currently no data are available.

2.6.2.3. Overview of applicability of lines of evidence to each plausible pathway

An overview of the applicability of each of the lines of evidence (LoE) to the four plausible pathways is presented in Table 2-19. When the lines of evidence are applied to each plausible pathway, the assessment concludes that pathways are either exceptionally unlikely (<1% probability for Pathway C) or extremely unlikely (<5% probability for Pathways A, B, and D). Expert judgement was used to synthesize the applicability (loosely, moderately, or highly) of all LoE into a final assessment. Further details about estimated probabilities are available in Appendix 7.

Line of evidence	Pathway A: Out of zone fracture growth	Pathway B: Direct intersection of water bore	Pathway C: Loss of well integrity	Pathway D: Direct intersection of natural fault
Plausible pathway conceptualisation	Picket server skiller Beserver of the Server skiller Picket server	Construction of the second of	The second secon	Constructions of the second se
Line of evidence 1: Basic hydraulic fracture growth and fluid transport models	Moderately applicable	Highly applicable	Highly applicable	Highly applicable
Line of evidence 2: Industry standard numerical hydraulic fracture and fluid transport models	Highly applicable	Highly applicable	Highly applicable	Highly applicable
Line of evidence 3: Analysis of samples from monitoring / water bores	Highly applicable	Highly applicable	Highly applicable	Highly applicable
Line of evidence 4: Remote fracture monitoring	Highly applicable	Highly applicable	Moderately applicable	Highly applicable

Table 2-19 Applicability of lines of evidence to each plausible pathway. Colour codes are as follows: highly applicable (green), moderately applicable (yellow), loosely applicable (orange).

Line of evidence Interpretation o pressure data	e 5: f injection	Loosely applicable	Moderately applicable	Loosely applicable	Moderately applicable
Final assesment for Gunnadah Basin (terminology as defined in Mastrandrea et al. (2010))	High agreement across experts and robust evidence support a "level of confidence" or "quantified measure of uncertainty"?	Yes, multiple, consistent an independent lines of high-quality evidence to support a quantified measure of uncertainty	Yes, multiple, consistent an independent lines of high-quality evidence to support a quantified measure of uncertainty	Yes, multiple, consistent an independent lines of high-quality evidence to support a level of confidence	Yes, multiple, consistent an independent lines of high-quality evidence to support a quantified measure of uncertainty
	Level of confidence or quantified measure of uncertainty (likelihood)	Extremely unlikely (<5% probability) with high confidence to extend vertically beyond 100m with parameters as defined in Appendix 7	Extremely unlikely (<5% probability) with high confidence to extend horizontally beyond 300m with parameters as defined in Appendix 7	High to very confidence that this pathway would be unlikely	Extremely unlikely (<5% probability) with high confidence to extend horizontally beyond 300m with parameters as defined in Appendix 7

2.6.3. Methodology for assessment of fate and transport pathways

2.6.3.1. Flow-path segmentation

The conceptual models underpinning the Level-2 assessments consider possible pathways for exposure and allow assessment of chemicals on the basis of comparing particle transport time to a receptor against time to degrade to a certain % of the initial concentration (e.g. 10 or 1%, depending on the toxicity category). Chemicals may be considered to present elevated exposure potential if they have more than a predefined % of their initial source concentration remaining at the target receptor (see e.g. recent work by Rogers et al. 2015.). The remaining concentration at a receptor can further be used to calculate so-called dilution attenuation factors (DAF). How much degradation will occur for a given chemical half-life depends on the chemical's transport time between source and receptor, which in turn depends on transport distance, groundwater velocity and geological attenuation for a defined pathway.

For the current study to provide a broad range of possible transport pathways across coal seam gas areas in Australia, the transport pathways and the corresponding travel time from a contaminant source to a receptor class has been calculated in two separate study areas. The first area uses an existing groundwater model developed for the Surat and Bowen basin in Queensland (OGIA model, QWC 2012) and used by CSIRO in the GISERA project (Janardhanan and Moore 2015). The second area is within the Gunnedah basin, New South Wales, and uses the groundwater model developed by CDM Smith (2014). The use of existing groundwater flow models ensures the assessment is cost-effective and fit-for-purpose while using best-practice methods.

Upper bound transport times between source and receptor are obtained by assuming the chemicals migrate unretarded through groundwater, i.e. no geological attenuation is assumed. This effectively means that the chemical velocity equals that of a water molecule. In a later stage of the assessment geological attenuation (sorption) will be added to the transport process in order to derive a more realistic concentration at a given receptor (see Section 5).

Because of the complexity of calculating transport pathways from a coal seam gas well environment via leakage pathways linked to wells, faults, or other features into adjacent aquifers, the total transport pathway is segmented into two individual segments (Figure 2-32). In this way different transport models or approaches may be used to derive the travel time in each segment separately. If indeed the transport time can be assessed in each of the individual segments, then total transport time is obtained from aggregation of the individual travel times for each segment.



Figure 2-32 Segmentation of a plausible flowpath involving flow through a leaky wellbore annulus (Segment A) and flow through a water bearing aquifer potentially intercepting a groundwater dependent ecosystem (Segment B).

The first segment involves the CSG well environment and considers chemical migration along four plausible pathways into overlying/underlying or nearby aquifers (Figure 2-32 and section 2.6.2). The second segment involves chemical migration through aquifers towards a groundwater-related receptor (Figure 2-32).

For example, consider the pathway "Fracture growth into an overlying aquifer" (for details see Section 2.6.2.1): this could involve a first segment from the fractured zone in a coal seam, the whole way up through an aquitard and loss of fluid into a high-permeability aquifer (the first segment ends at the aquitard/aquifer interface). This is then followed by a second segment involving transport from the aquitard/aquifer interface towards a potential receptor (water bore at a given distance defined by the spatial analysis).

For the first segment, the study conservatively assumes that an unspecified but significant fraction of the injected hydraulic fracturing fluid will travel through each of the plausible pathways and reach the nearest aquifer.
 Theoretically, this fraction would generate a solute plume where the fluid enters a permeable aquifer. The assessment further assumes, conservatively, that the solute is transported instantaneously from its injection

point to the point where the pathway discharge into an aquifer. In other words, the travel time is effectively zero. In other words, chemical concentrations along the first segment are not calculated, as only particle tracking for the second segment will be undertaken.

• To calculate the subsequent migration of such solute plume through the second segment (i.e. aquifer), a much finer spatial discretisation would be required in comparison to the corresponding flow model (mainly to limit numerical dispersion). Much more simplified but still fit-for-purpose particle tracking simulations are undertaken to derive the travel time of a water molecule; this travel time is subsequently adjusted for chemical/biological and geological attenuation using data from Chapter 4.

2.6.3.2. Solute particle tracking

This study uses existing groundwater models and applies particle tracking with MODPATH (Pollock 2012) to determine travel time of water particles (as proxies for chemical substances) in groundwater (i.e. the second segment of a chemical's pathway) and subsequently adjusts the chemical's travel time for any relevant attenuation process (Figure 2-33). Particle-tracking analysis are commonly used for mapping the recharge-contributing area to pumping wells (US EPA 1994a) and for obtaining transit times of groundwater at the discharge point (McGuire and McDonnell 2006; Gusyev et al. 2014). The MODPATH generated transit times represent the time taken by groundwater molecules to travel in groundwater from the starting cell, e.g. the groundwater recharge area at the aquifer top, to an outlet cell such as a pumping well or a spring (Boronina et al. 2005; McGuire and McDonnell 2006; Sanford, 2010).

MODPATH is a particle-tracking post-processing model that computes three-dimensional flow paths using output from groundwater flow simulations based on MODFLOW (Harbaugh 2005). The program uses a semi-analytical particle-tracking scheme that allows an analytical expression of a particle's flow path to be obtained within each finite-difference grid cell. A particle's path is computed by tracking the particle from one cell to the next until it reaches a boundary, an internal sink/source, or satisfies another termination criterion. Output from steady-state or transient MODFLOW groundwater flow simulations is used in MODPATH to compute paths for imaginary "particles" of water moving through the simulated groundwater system. In addition to computing particle paths from the point of release until its final location, MODPATH computes the time of travel for particles moving through the system. The particle travel or residence time represents the velocity of a non-reactive chemical (no interaction with the solids) due to flowing groundwater; the effect of hydrodynamic dispersion and molecular diffusion on solute migration is neglected. A simplified way to account for the effect of dispersion and diffusion on dilution is by implementing an analytical solution of the three-dimensional advection-dispersion model for given particle pathways (see Section 5.2.1.3).

The accuracy of numerically-generated pathlines, and a proper interpretation of what they represent, depends on the extent to which the groundwater system can be realistically represented by a discrete network of finite-difference or finite-element cells. The degree of spatial discretization in a finite-difference model influences:

- the level of detail at which hydrogeologic and system boundaries can be represented,
- the accuracy of velocity calculations,
- the ability to accurately and unambiguously represent internal sources and sinks.

In this study pre-existing models built for analysing pressure changes in aquifers due to CSG development were used for undertaking particle tracking analyses. While these models are fit-for-purpose, the accuracy of the tracks could be improved by using finer-resolution models, particularly for the receptors closer to the CSG wells



Figure 2-33 3D transient example illustrating forward pathlines released adjacent to the constant head cells (coloured in red) in the top layer 1. Note that some pathlines track through the discontinuous aquitard in middle layer 2 (coloured as solid green), and reach the water supply well in bottom layer 3.

Particles are stopped whenever they reach points of termination or whenever the cumulative tracking time equals the maximum allowed value. A particle terminates when:

- it reaches an external boundary face or an internal sink/source cell that captures the particle,
- it enters a cell with a zone code that designates the cell as a termination location,
- the cumulative tracking time has reached the maximum allowed value, or
- it encounters an abnormal condition that will not allow tracking to continue.

Sometimes it is useful to stop particles at an arbitrary location that does not correspond to a natural termination point (e.g. the boundary of a CSG project area). MODPATH provides that capability by allowing zone numbers to be assigned to grid cells and identifying a range of zone numbers that indicate particle termination locations. An example of such a situation would be a case where the desire is to determine the recharge locations at the water table that contribute water to a deep aquifer. That could be achieved by assigning a zone number to the cells representing the deep aquifer, indicating they are termination points. Particles that start at the water table would then stop when they reach the deep aquifer because the cells are designated termination locations (Pollock 2012).

Particle tracking may evolve in two ways: either so-called "backtracking" is done starting from a selection of receptors working backwards to identify which part of the aquifer is connected to the receptor and what the travel time is, should there be a connection, or the tracking starts at the contaminant source and moves forward to identify pathways that may intersect a receptor. The latter is called "forward tracking". Forward tracking is used first here to determine how far particles will theoretically travel when released within the coal seam gas well area. Within this zone of influence, the relevant receptors are then selected for a backward tracking analysis to determine if any pathway exists with one or more coal seam gas wells. Note that a pathway is considered to exist when the particle intersects model grid cells that contains a coal seam gas well. This does not automatically mean that there is actually a connection between the receptor and the coal seam gas well. Another reason to use a backward tracking analysis is that it allows the particles to be released in the exact (x, y, z) locations of any receptor within a grid cell.

This analysis will be undertaken using existing best-practice models (i.e., a subdomain of the original OGIA model for the Surat (QWC 2012), and the CDM Smith (2014) groundwater model for the Gunnedah basin), at a minimum effort. The main limitation of both models is their coarse spatial discretisation. The current 2012 OGIA¹⁰ model has a 1.5x1.5 km² horizontal discretisation and limited vertical resolution (e.g., Figure 2-34), while the CDM Smith model has a 1x1 km² grid: both grids

 $^{^{10}}$ A new model has been published in 2016 (OGIA 2016), but was not available at the time this analysis was undertaken. This model still has a fairly coarse horizontal discretisation, but incorporates more processes (e.g. multiphase flow) and more hydrogeological data. The Walloon Coal Measures are represented by 3 numerical layers and the Hutton Sandstone by a single numerical layer.

are too coarse to evaluate short-distance pathways or to relate particle end points to specific locations of receptors within a grid cell (that is in a forward tracking analysis).



Subdomain of OGIA model for particle tracking

Figure 2-34 Stratigraphy of the Surat basin (QWC 2012). For pathway B particles will be released in the Walloon Coal Measures (WCM) subdomain (red box); for pathways A, C and D particles will be released in aquifers above the WCM aquitard.

Realistic travel times will be obtained by applying the above simulators to each of several possible pathways, including the wellbore failure scenario¹¹ (leaky wells and offset wells), fracture growth into a well, fracture growth into an overlying aquifer, well rupture during injection, and fracture growth into a fault. Such scenarios have also been identified by the US EPA (2016a) as possible failure scenarios that can lead to contamination of groundwater resources following hydraulic fracturing operations.

The analysis considers pathways at an individual well but will also consider an entire well field to capture possible cumulative effects from mass accumulating in hundreds and possibly thousands of hydraulically fractured wells – this involves superposition of sources that contribute to the same receptor.

2.6.4. Particle tracking analysis for the Gunnedah basin

2.6.4.1. Hydrogeology

The study area was selected where an existing numerical groundwater flow model was available, considered fit-forpurpose to provide estimates of solute particle pathways between deep groundwater sources of CSG chemicals and

¹¹ Based on previous work of CSIRO, including Bunger et al. 2010.

groundwater receptors. Based on a LeapfrogHydro geological model (CDM Smith 2014), a MODFLOW–SURFACT model was developed by CDM Smith (2014), covering a total area of 53,219 km². The spatial interpolation of geological data was undertaken using a proprietary approach based on radial basis functions (Beatson and Newsam 1992). For groundwater flow simulation, the geological domain was discretised using a combination of 1 km² and 5 km² cells into 238 rows and 126 columns. The model featured 24 layers and a mixture of specified flux (i.e., Neumann) and hydraulic head-dependent (i.e., Cauchy) boundary conditions. The discretisation of model layers is shown Table 2-20. For this model, the aquitard sequence overlying the Hoskisson Coal represents the key aquitard that will affect the vertical propagation of hydraulic stresses induced in the underlying coal seams by CSG production to the overlying Pilliga Sandstone aquifer.

Geological model layers represented either a single geological unit (e.g., Pilliga Sandstone) or a combination of multiple units (e.g., layer 9) (Table 2-20). Before the numerical discretisation of the geological layers (column 2) was undertaken, further aggregation was applied (column 3). For example, geological layers 5 to 9 (representing 11 geological units) were combined as single aquitard (based on the geological model, the thickness ranged from 5 m to 1045 m). The deeper aquitard is composed of layers 14 to 19 (based on the geological model, the thickness ranged from 2 m to 867 m). Numerical discretisation of the resulting hydrostratigraphic units was subsequently undertaken (column 4). For example, the single aggregated aquitard between the Pilliga Sandstone and the Hoskissons Coal was divided into six groundwater model layers. The thickness of model layers used to represent aquitards adjacent to CSG reservoirs was increased exponentially with increasing vertical distance from the reservoir units. This method of discretisation was undertaken for the following reasons, as described by CDM Smith (2014). The use of a single model layer to represent an aquitard implies a constant vertical hydraulic gradient in the aquitard. It also results in the near-instantaneous release of stored water throughout the full thickness of the aquitard in response to a decline in hydraulic head in an adjacent aquifer. Instead, aquitards can be represented using multiple model layers, which are able to simulate the propagation of a change in vertical hydraulic gradient through the aquitard over time more appropriately. The change in gradient then results in the gradual release of stored water. An exponential discretisation scheme, in which aquitard layers adjacent to a coal measure are thinnest, is best able to propagate changes in vertical hydraulic gradients and the release of stored water.

CDM Smith (2014) stated that "current geological evidence indicates that Permian to Triassic age faulting in the Gunnedah Basin is unlikely to provide conduits for preferential flow of water and hydrocarbons between the target coal seams and shallow groundwater sources in the overlying Surat Basin¹² and Namoi alluvium". For this reason, geological faults were not represented in the model. More specifically, the authors cite an earlier study which concluded that no evidence exists for the presence of large, post-Jurassic age faults. Where present, displacement of Jurassic (and younger) strata was found to be minor. The assumption by CDM Smith (2014) that faults do not impact groundwater flows in the Gunnedah Basin is also consistent with the conceptualisations presented in other studies, such as Schlumberger Water Services (2012) and the Bioregional Assessments Programme (in preparation).

For the purpose of particle tracking analysis the main hydrostratigraphic unit of interests are the Pilliga Sandstone (represented by a single numberical layer) and the Alluvium (single numberical layer) that may be in contact with the Pilliga Sandstone in locations where the aquitards composed of Bungil-Mooga-Orallo Formation and the Liverpool Rance Volcanics-Wallumbilla Formation are absent.

In the study area, the Pilliga Sandstone is a confined aquifer where it is overlain by an aquitard, either the Blythesdale Group (the lateral equivalent of the Orallo Formation, Mooga Sandstone and lowermost Bungil Formation of the Surat Basin in NSW) or Liverpool Range Volcanics. The Pilliga Sandstone is an unconfined aquifer in the outcrop areas, to the south-east of the Narribri Gas Project Area (Figure 2-35). The surface geology further comprises of quaternary colluvium and aolian (collectively named the Alluvium) and the Blythesdale Group. In the northern edge of the study area, the Alluvium is in contact with the Pilliga Sandstone (Figure 2-36 and Figure 2-37). The Blythesdale Group and the Alluvium are overlying the Pilliga Sandstone across the majority of the project area (apart from the southeast corner, Figure 2-35). The Blythesdale Group sediments contain off-white, coarse-grained, cross-bedded, well-sorted, porous, sandstone and

 $^{^{12}}$ This includes the Pilliga Sandstone, Purlawaugh Formation and Blythesdale Group

conglomerate, nterbedded with minor shale, siltstone and coal (CDM Smith 2014). The thickness of the Blythesdale Group in the project area ranges from 0 to 88 m with an average of 46 m thick (CDM Smith 2014).

Geological unit	Geological model layer	Hydrostratigraphic unit	Groundwater model layer(s)
Cenozoic Alluvium	1	aquifer	1
Liverpool Range Volcanics	2		2
Wallumbilla Formation	2		3
Bungil Formation		aquitard	4
Mooga Sandstone	3		_
Orallo Formation			5
Pilliga Sandstone	4	aquifer	6
Purlawaugh Formation	5		7
Garrawilla Volcanics	6		0
Deriah Formation	_	_	8
Napperby Formation	/		•
Digby Formation	8		9
Trinkey Formation		aquitard	
Wallala Formation		-	10
Breeza Coal Member			11
Clare Sandstone	9		
Howes Hill Coal Member			_
Benelabri Formation			12
Hoskissons Coal	10	CSG reservoir	13
Brigalow Formation		_	14
Arkarula Formation	11	<u>-</u>	15
Melvilles Coal Member	11		16
Pamboola Formation		aquitard	17
Watermark Formation	12	_	18
Porcupine Formation	12		19
Maules Creek Formation		intorburdon	20, 21
(upper)		Interburgen	20, 21
Maules Creek Formation	13	CSG reservoir	22
Maules Creek Formation (lower)		interburden	23, 24

Table 2-20. Summary of geological units, hydrostratigraphic units and groundwater flow model layers represented in the Gunnedah Basin groundwater flow model.



Figure 2-35 Surface geology of the study area (modified from CDM Smith 2014). Red polygon represents study area.

At the western edge of the study area the Rolling Downs (Wallumbilla Formation) sediments (considered an aquitard in CDM Smith 2014) overly the Blythesdale Group (Figure 2-36 and Figure 2-38). Therefore, in the western part of the study area the Pilliga Sandstone is indeed a confined aquifer overlain by an aquitard composed of Rolling Downs and Blythesdale Group. Where the Pilliga Sandstone is a confined aquifer there would be no direct pathways to water-dependent assets at the land surface, except for water bores that are screened in the Pilliga Sandstone aquifer.

In the particle tracking analysis the Pilliga Sandstone is considered to contain the particle sources at the base of the formation, i.e. at the interface with the underlying aquitard (e.g. Purlawaugh Formation). Because the Pilliga Sandstone is one of the most important groundwater resources in the Gunnedah Basin, groundwater abstraction points situated within this aquifer will be considered as receptors and treated as sinks in the particle tracking calculations. A second series of receptors is situated within the area where the alluvium is in concact with the Pilliga Sandstone (Figure 2-37) or where the Pilliga Sandstone outcrops (Figure 2-39): these receptors will constitute a second set of sinks for the particle tracking calculations.



Figure 2-36 Lithology map and cross-section locations (CDM Smith 2014). Red polygon represents study area.



Figure 2-37 Geological model cross-section A-A' (CDM Smith 2014).



Figure 2-38 Geological model cross-section B-B' (CDM Smith 2014).



Figure 2-39 Geological model cross-section C-C' (CDM Smith 2014).

2.6.4.2. Groundwater flow model

A regional-scale numerical groundwater flow model of the Gunnedah Basin developed by CDM Smith (2014) has been the basis of the present study. The study area contains coal seam gas reserves associated with Early Permian coal seams of the Maules Creek Formation and secondary gas reserves associated with coal seams of the Late Permian Black Jack Group (contains the Hoskissons coal seam, Table 2-20). The groundwater model was used by CDM Smith to predict the potential impacts on groundwater resources within the groundwater impact assessment study area due to water extraction from the coal seams that will be targeted for coal seam gas production. Simulations of water extraction from the coal seams provided regional -scale predictions of depressurisation and drawdown of hydraulic head within the Gunnedah Basin and the associated induced flows between groundwater sources and hydrostratigraphic units. The same model has been used in this study to generate additional information in terms of hydraulic heads across all relevant formations in areas of greatest expected drawdown.

The groundwater model is a MODFLOW–SURFACT model, covering a total area of 53 219 km². For groundwater flow simulations, the geological domain was discretised using a combination of 1 km², 5 km² and 25 km² cells into 238 rows and 126 columns (see Figure 2-40 for the model grid in X-Y direction). A total of 24 geological model layers are represented (Table 2-20). Coal seam gas production was simulated using time-varying specified flux (i.e., Neumann) boundary conditions. For this model, the aquitard sequence overlying the Hoskisson Coal represents the key aquitard that will govern the vertical propagation of hydraulic stresses induced in the underlying coal seams by coal seam gas production to the overlying Pilliga Sandstone aquifer. In 15 locations (so-called observations) the vertical head distribution pre- and post-production will be interrogated and used to provide detailed information about hydraulic head gradients that exist

between the hydrocarbon reservoir and the main aquifers (see next section). The post-production times are 26, 100, 200, and 500 years since commencement of production (production is assumed to last for 26 years, hence the first timestep is at the end of gas production). Stresses (specified as fluxes) after the 26-year production period are put to their preproduction values.

Model cells featuring negative recharge values were assumed to represent the locations of groundwater extraction. Groundwater extraction by water bores was not implemented in the model explicitly; instead, a spatial distribution of recharge in the Namoi Alluvium area was estimated through calibration of the model to observed hydraulic heads. Calibrated recharge values across the Namoi Alluvium area (which intersects part of the study area) ranged from < -0.5 mm/d to < +0.5 mm/d. In practice, these cells may represent a single bore or the sum of many bores. As a result, this approach does not simulate flow paths to individual bores. Instead, the total extraction within a given model cell was removed from the centre of the cell, regardless of the location of a bore within that cell. Particle tracking results are therefore considered to be meaningful at regional scales (i.e. the model grid encompassing the study area and its surroundings) rather than local scales (i.e. individual model cells). CDM Smith (2014) adopted an approach whereby groundwater extraction was not directly simulated in the model. This is justified as the model calibration did not involve modification of hydrogeological properties; rather groundwater fluxes were calculated at the water table based on prescribed head data (CDM Smith 2014). The resulting estimates of net groundwater recharge to the alluvium include groundwater pumping. Therefore, the net recharge rate can have negative values in areas where the aquifer is over used and total discharge exceeds total recharge. Any cone of depression that would potentially exist in the Pilliga Sandstone will not divert particles towards a water bore; rather, particles will travel across cells with water bores and will terminate in a cell at ground surface. The problem of particles not being intercepted by water bores was circumvented by the use of backward (rather than forward) particle tracking analyses. Particles were released in Pilliga Sandstone aquifer cells that had known locations of water bores and subsequently tracked along ambient groundwater flow paths until it reaches its point of origin (see further in Section 2.6.4.4).

The difference in head between the production interval and water bearing aquifers is a key variable controlling the rate of leakage through failed wells/bores. Two distinctively different cases need consideration: i) natural gradients, which are usually small across aquitards, and ii) anthropogenically enhanced gradients, which may be high, especially in productive CSG well fields. Furthermore, high residual head differences that exist after CSG production ceases, may generate relatively high flow rates through any leaky wells/bores, exploration bores or natural faults.

Prior to CSG production, the hydraulic head distribution in a vertical cross-section comprising an aquitard separating a coal seam gas target formation from a beneficial aquifer can be one of the three following conditions:

- nearly identical heads resulting in a negligible hydraulic gradient across the aquitard,
- hydraulic gradient is from the production zone to surficial water bearing aquifers,
- hydraulic gradient is from the surficial aquifers to the CSG production zone.

In addition to these three location-specific conditions, the hydraulic head gradient prior to production may vary within a single CSG development zone. As an example, the MODFLOW-SURFACT groundwater model used in the CDM Smith (2014) study was interrogated to find the hydraulic gradients pre- and post production for fifteen observation locations (Figure 2-40 and Figure 2-41) around the location of greatest expected drawdown. The model includes a total of 425 proposed production well pairs, providing access to primary (Maules Creek Formation) and secondary (Black Jack Group including Hoskissons Coal) coal seam gas targets. The typical distance between bore pairs is about 1 km.



Figure 2-40 Location of the fifteen observation points within the model domain including the study area. A close-up of the location of proposed CSG wells is provided in Figure 2-41.

For the northern observation points (Figure 2-44, graphs 1 to 5), the hydraulic gradient is upward, i.e. from the deeper aquifers and production zone (dark blue) to the surficial aquifers (purple). This may be due to irrigation pumping from the relatively shallow Pilliga Sandstone aquifer. In the southern observation points (Figure 2-44, graphs 11 to 14), the gradient is downward, suggesting recharge and movement of water from the surficial aquifers to the production zone. The magnitude of head differences ranged from 30 metres upward to 50 metres downward. This translates to a hydraulic gradient of 0.03 m/m upward and 0.07 m/m downward, respectively.



Figure 2-41 Location of the CSG wells within the study area.

Greater head gradients in a downward direction, up to three times those of pre-production levels, are seen immediately after production ceases (Figure 2-45). In some cases the hydraulic gradient has reversed (e.g. cell (56, 77)), with water now seeping into the coal seam target formations whereas under the pre-production gradient seepage was likely upward. The gradients continue to recover beyond 100, 200 (Appendix 2) and 500 years (Figure 2-46). However, even after 500 years, the hydraulic gradient has not returned to pre-production levels. In some instances, upward gradients continue to exist throughout the entire pre- and post-production period, e.g. in cell (36, 47), suggesting flow from the coal formations to the Pilliga Sandstone aquifer may occur provided a pathway for flow exists.



Figure 2-42 North-South model cross-section along model column 67 showing discretisation of hydrostratigraphic units and location of the observation points along a model transect. Pilliga Sandstone aquifer outcrops near row 76.



Figure 2-43 Model cross-section along model row 76 showing discretisation of hydrostratigraphic units and location of the observation points along a model transect. Pilliga Sandstone aquifer outcrops near column 77 [indicate column on fig 10 and add cross-section near column 67].







Figure 2-45 Hydraulic head gradients immediately post CSG production (26 years after commencement) for cells of the study area, with formations described in Figure 2-43.



Figure 2-46 Hydraulic head gradients 500 years after commencement of CSG production for cells of the study area, with formations described in Figure 2-43. CSG production lasted for 26 years.

The MODFLOW-SURFACT model was also used to produce timeseries of predicted changes in hydraulic head for cells with the highest overall drawdown due to CSG production in the primary (early Permian) coal targets of the Maules Creek Formation (Figure 2-47), and secondary targets (late Permian) of Hoskissons Coal (Figure 2-48). This was compared with the hydraulic heads of the confined Pillinga Sandstone aquifer (a major regional aquifer in the study area). The head difference between the Maules Creek Formation production interval and water bearing aquifers due to CSG production was up to 140 metres, but this declined rapidly over 100 years to around 40 metres head difference, and returned to pre-CSG extraction levels after around 1,000 years. The difference for production in the Hoskissons Coal formation was less, at 28 metres, but it also returned to pre-development levels after around 1,000 years. The examples shown all produce a downward gradient, presenting a condition that potentially leads to long-term head loss from the Pilliga Sandstone should preferential flow paths exist due to loss of well integrity.



Figure 2-47 Changes in hydraulic head for cells in the region of highest drawdown in the Maules Creek Formation, compared with heads in the confined Pillinga Sandstone aquifer. Start date (t = 0) corresponds commencement of 26-year CSG production period. Inset shows negligible head variation in Pilliga Sandstone.



Figure 2-48 Changes in hydraulic head for cells in the region of highest drawdown in the Hoskissons Coal formation, compared with heads in the confined Pilliga Sandstone aquifer. Start date (t = 0) corresponds commencement of 26-year CSG production period. Inset shows negligible head variation in Pilliga Sandstone.

2.6.4.3. Forward particle tracking analysis

2.6.4.3.1. Verification of 30 km buffer zone

A 30 km buffer area around the study area had previously been used by CDM Smith (2014) as a focus area for groundwater impact assessments. The same buffer area was used in the current study to limit the spatial analysis to an area large enough to capture all pathways identified through particle tracking analysis. To test whether the buffer area was indeed sufficiently inclusive of all pathways, a limited particle tracking analysis was undertaken by releasing particles from the main corner points of the study area, rather than from individual wells (Figure 2-49). By using the main corner points it is assumed that CSG wells would be located on the boundary of the study area and therefore maximum pathway lengths would be achieved. An assessment of pathways for the proposed CSG well locations is provided in Section 2.6.4.3.3. Release depths range from 25 to 296 m with a mean depth of 141 m. Based on these calculations, all of the particles' end point are within the buffer zone (the buffer zone is located outside the frame of the graph). Where no pathways emerge from the study area boundary, it is assumed that groundwater flows are stagnant at these cells (Figure 2-49).



Figure 2-49. Particle tracking path lines (black), originating from selected cells (red) on the study area boundary (yellow) and 30 km buffer zone. Particles are released from the Pilliga Sandstone aquifer. Model cells are 1 × 1 km².

2.6.4.3.2. Baseline case without hydraulic fracturing

Particle tracking analysis is undertaken in two steps: first a baseline case is considered that reflects the groundwater pathways prior to any hydraulic fracturing operations. In the second step new pathways are considered as a result of hydraulic fracturing.

The baseline case explores whether any naturally occurring flowpaths exist between the main coal formations and the overlying aquifers. For the Gunnedah Basin, the analysis involves releasing particles within the Maules Creek coal layer and tracking their pathway until their final position (see Figure 2-42 and Figure 2-43 for location of the Maules Creek coal target seams in the stratigraphic column). In this calculation no hydraulic fracturing induced pathways exist between the coal layers and the aquifers.

To constrain the analysis to the region where most of the particle movement would occur, a total of 425 CSG well locations were inputted into the groundwater flow model. Note that the wells do not abstract groundwater therefore do not influence the groundwater flow; their sole purpose is to define particle sources to areas that could see hydraulic fracturing fluids during the production phase. The locations are consistent with those used for the assessment of groundwater depressurisation associated with CSG extraction (CDM Smith 2014). A forward solute particle tracking analysis was then undertaken by releasing particles in each model cell containing a CSG well (Figure 2-50). This forward analysis has its particle source at each of the 425 CSG wells while the sinks will be model cells identified by following groundwater flow lines until they reach a natural discharge zone, or another feature that ends the pathway (see further in Section 2.6.4.3.3).



Figure 2-50 Forward particle tracking pathlines from 425 CSG wells. Particles are released at the base of the Maules Creek Coal, with one particle released for each well.

Theoretically particles may end their path in different types of sinks; the following categories of sink cells are considered in MODFLOW:

- river package cells representing rivers,
- evapotranspiration package cells,
- (negative flux) recharge package cells.

A histogram of travel times based on 425 particles travelling from their source to a particular sink is provided in Figure 2-51. All particles ended their path in so-called weak sinks. Modpath defines "weak" sinks as: sinks that do not remove water at a rate sufficient to remove all of the water that enters a cell. The existence of weak sinks appears to be a result of coarse spatial discretisation, although other factors could also be involved. More generally, from visual inspection of the particle travel paths (and exit locations) it appears that the particles mostly exit the model once they have reached close to

land surface (possibly the water table elevation and ET sinks). For a detailed discussion of weak sinks, see Abrams et al. (2013).



Figure 2-51 Histogram of particle travel times for 425 sources (i.e. CSG wells) released within the Maules Creek Coal (base). Also shown are the 10th, 50th and 90th percentile values (dashed vertical lines) and the cumulative probability (blue line).

Table 2-21 Particle tracking sink formations and travel time statistics for particles released within the Maules Creek Coal.

Particle tracking sink formation	Frequency (%)	Travel time statistics (year)
Namoi Alluvium	100	Min: 530,998
		Max: 13,205,108
		Mean: 4,400,192
		Stdev: 2,178,058

An alternative representation of the results from the particle tracking calculations is given in Figure 2-52 and Figure 2-53. These plots show the time the particles reside in the different formations. Particles released in the Maules Creek coal formations travel across the Permian aquitard formations, albeit very slowly. They generally end up in the Alluvium after having travelled through the Pilliga Sandstone. Travel times into the Namoi Alluvium are extremely long, on average more than 4 million years (Table 2-21); this is due to the very long particle residency time within the aquitards (because the flow velocity across such aquitards is nearly zero, chemical transport is by diffusion, see e.g. Smith et al. 2016). Travel time and distance statistics for the same particles as they passed through the Maules Creek Formation are provided in Table 2-22. It should be noted that the average time spent travelling through the Maules Creek Formation by a particle was less than one percent of the average total travel time.

Table 2-22 Particle tracking travel time and distance statistics for particle pathways within the Maules Creek Coal.

Particle tracking formation	Travel time statistics (year)	Travel distance statistics (km)
Maules Creek	Min: 396 Max: 9,593 Mean: 3,629 Stdev: 2,132	Min: 0.11 Max: 32 Mean: 10 Stdev: 5.96



Figure 2-52 Hydrostratigraphic units encountered during particle tracking for particles released in Maules Creek (top: particles for wells 1 to 200; bottom: particles for wells 201 to 425). The bottom graph has units of 10⁷ years.



Figure 2-53 Hydrostratigraphic units encountered during particle tracking for particles released in Pilliga Sandstone (top: particles for wells 1 to 200; bottom: particles for wells 201 to 425).

2.6.4.3.3. Hydraulic fracturing induced pathways

In this section particle tracking analyses are undertaken under the assumption that due to hydraulic fracturing additional pathways have been generated that connect the hydraulically stimulated coal formations with overlying aquifers. Note that the model was not constructed in a way that allows modelling the release of particles from target coal measures into the overlying aquifers. Rather a connection pathway had to be assumed within the model and particles manually "released" into the bottom of the overlying aquitard where the flow pathway is assumed to connect with the aquitard (also see the discussion in Section 2.6.3.2). The conditions under which such connections can potentially exist are discussed in section 2.3.

Calculated pathways for particles released in the Pilliga Sandstone are shown in Figure 2-54; a total of 425 particles were released at the presumed future locations of the wells at the centre of each model cell. Many of the particles' pathways end within the study area, also confirming that the 30 km buffer zone considered for the analysis is appropriate. Only a few particles exit the studay area across the northern boundary (Figure 2-55). Further images with particle tracking pathlines are shown in Figure 2-56 to Figure 2-58. These cross-sectional views illustrate, for instance, existence of a few pathways into the Namoi alluvium. The cumulative frequency distribution of the particles' travel time, for particles released in the Pilliga Sandstone, is shown in Figure 2-59, while the statistics of the particles' sinks (i.e. the aquifers in which the pathways end) and particle travel times are summarised in Table 2-23.



Figure 2-54 Forward particle tracking pathlines from 425 CSG wells (assumed located in the middle of each pink cell) within the NGP area. Particles are released in the Pilliga Sandstone, with one particle released for each pink cell (half-way the cell height). Also shown is the 30 km-radius boundary around the study area (black boundary). A more detailed depiction of particle travel paths is provided in Figure 2-59.



Figure 2-55 Forward particle tracking pathlines from 425 CSG wells (assumed located in the middle of each pink cell). Particles are released in the Pilliga Sandstone, with one particle released for each pink cell (half-way the cell height).



Figure 2-56 Hydrogeological model units with location of grey-shaded cross-section capturing a single pathline (for details, see Figure 2-57).



Figure 2-57 Example solute particle pathline released in the Pilliga Sandstone (forward calculation). Modelling shows this particle pathway ending in the Namoi Alluvium.



Figure 2-58 Forward particle tracking pathlines from 425 CSG wells. Particles are released at the middle (top) and base (bottom) of the Pilliga Sandstone. One particle is released for each well.



Figure 2-59 Histogram of particle travel times for 425 sources (i.e. CSG wells) released within the Pilliga Sandstone aquifer (middle). Also shown are the 10th, 50th and 90th percentile values (dashed vertical lines) and the cumulative probability (blue line).

Particle tracking sink formation	Hydrostratigraphic classification	Frequency (%)	Travel time statistics (year)
Namoi Alluvium	Surficial aquifer	56	Min: 2,332 Max: 50,390 Mean: 19,158 Stdev: 11,752
Pilliga Sandstone	Confined aquifer	32.2	Min: 2,201 Max: 88,741 Mean: 9,919 Stdev: 12,611
Rolling Downs Group (also includes Blythesdale Group aquifer)	Aquitard; separates Pilliga Sandstone aquifer from Namoi Alluvium aquifer	11.8	Min: 160 Max: 15,709 Mean: 4,901 Stdev: 3,460

Table 2-23 Forward particle tracking sink formations and travel time statistics for particles released within the Pilliga Sandstone.

The relatively short minimum travel time in the Blythesdale Group represents pathways where this Group forms a very thin outcropping layer.

2.6.4.4. Backward particle tracking analysis

Backward particle tracking was undertaken to identify pathways between receptors (referred to as assets in Section 2.4 and 2.5) nearby the study area and potential locations of CSG wells within the study area. In the case of backward tracking analysis, the particle travel path is calculated as starting from a receptor and travelling backwards (i.e. upgradient) to its point of origin. The point of origin could be a recharge area, or a source area where water and/or chemicals are entering the aquifer (e.g. through an injection well). The particle tracking is based here on a steady-state flow field that represents the natural groundwater flow system, i.e. not impacted by depressurisation. This flow condition represents the most conservative condition, as particles can travel away from a hypothetical CSG well location without being trapped within the depressurisation cone typically present around a CSG well field. Indeed, a flow field that is affected by CSG depressurisation would feature groundwater flow paths oriented towards CSG wells, not away from them. Under those conditions, any contamination would be unlikely to travel beyond the depressurisation cone. The receptors are located in the Namoi Alluvium (885), the Rolling Downs Group (324), and in the Pilliga Sandstone Pilliga Sandstone (49) (see Appendix 3 for further details); flow paths are tracked through those three aquifers. All receptors belong to the economic assets group (groundwater bores and surface water features such as water extraction points along creeks, see Section 2.4.2).

The results of particle tracking analyses are known to be particularly sensitive to the precise three-dimensional initial position of each particle. For this reason, the backward particle tracking analysis was undertaken twice. In the first analysis (hereafter the "top" approach), particles were released at the top of the cell representing a potential receptor. The results of this approach are consistent with groundwater flow paths that terminate at ground surface. Such flow paths may provide a groundwater source to receptors such as rivers, lakes and wetlands. A second analysis (hereafter the "bottom" approach) was undertaken in which particles were released at the bottom of the cell representing a potential receptor. The results of this approach are consistent with groundwater flow paths that terminate below ground surface; for example, at receptors such stock and domestic or town water supply bores.

Both analysis approaches proceeded according to the following steps. First, a total of 1267 potential receptors were identified within a 30 km radius of the study area, the majority of which were located outside the study area, though some were located within the study area (Figure 2-60). A single particle was used to represent each of these receptors. In order to ensure convergence of the semi-analytical particle tracking algorithm used, a total of 59 and 26 particles were subsequently omitted from the "top" and "bottom" approaches, respectively. As shown in Figure 2-60, most travel paths do not enter the study area and hence for those receptors the current model indicates that groundwater flowing towards these receptors will not have been in contact with chemicals originating from within the study area.

In the second step, only particles whose pathlines were found to originate within the study area (i.e. 86 and 107 particles for the "top" and "bottom" approaches, respectively) were retained (Figure 2-61). For each pathline the total travel time between point of release (receptor locations) and source was evaluated: the results showed that the majority of pathlines had extremely long travel times (>10⁷ years), even though receptor and source were located within a short distance of one another. This was due to the significant lengths of time required for particles to pass through low permeability aquitard units. Receptor-source pairs with such extremely long travel time were subsequently omitted from the data set.

Receptor-source pairs with travel times less than 10⁵ years (i.e. 25 and 34 particles for the "top" and "bottom" approaches respectively) are shown (Figure 2-62). The distributions of travel times were then classified using four groups; i.e. from 0 to 100 years, from 100 to 1,000 years, from 1,000 to 10,000 years, and from 10,000 to 100,000 years. For each receptor-source pair, the linear distance or proximity was determined as is shown in Figure 2-63. Proximity statistics (mean, standard deviation) were calculated for each group (Table 2-24).


Figure 2-60 Pathlines between all 1267 receptors and source locations (any starting point of a groundwater flow path) calculated using backward particle tracking for (a) "top" and (b) "bottom" approaches. A total of 951 and 983 particles are shown for the "top" and "bottom" approaches, respectively (with one particle released per receptor).



Figure 2-61 Pathlines between receptors (connected to sources within the study area) and source locations (any starting point of a groundwater flow path) calculated using backward particle tracking for (a) "top" and (b) "bottom" approaches. A total of 87 and 107 receptor-source pairs are shown for the "top" and "bottom" approaches, respectively (one particle released per receptor).



Figure 2-62 Pathlines between receptors and source locations (any starting point of a groundwater flow path) with travel time less than 10⁵ years calculated using backward particle tracking for (a) "top" and (b) "bottom" approaches. A total of 631 and 253 receptor-source pairs are shown for the "top" and "bottom" approaches, respectively (one particle released per receptor).



Figure 2-63 Proximities between receptors and source locations (any starting point of a groundwater flow path) for travel times less than 10⁵ years for (a) "top" and (b) "bottom" approaches. A total of 631 and 253 receptor-source pairs are shown for the "top" and "bottom" approaches, respectively (one particle released per receptor).

Comparisons between the results of the "top" and "bottom" approaches (Table 2-12) highlight the sensitivity of particle tracking results to initial particle locations. Particles released at the top of cells containing a receptor were associated with

relatively short travel time; i.e. less than 1,000 years, with most particles (20 of 24) less than 100 years. In comparison, particles released at the bottom of cells containing a receptor were associated with much longer travel times; i.e. up to 100,000 years. The distribution of travel times was evenly dispersed across the four classes, with each class representing no less than 18% (i.e. 6 of 34) of the total distribution. These results are consistent with the accepted understanding of nested groundwater flow systems in surficial aquifers (Tóth 1962, 1963). Particles released at the surface are more likely to encounter shallow, local scale groundwater flow paths. Conversely, particles released in the subsurface will encounter deeper, longer groundwater flow paths.

For the purpose of dilution and attenuation calculations, the minimum travel time of 10 years was combined with the minimal travel distance of 0.5 km to derive a particle velocity of 0.14 m/day. Note this is not the overall maximum velocity encountered in the area; based on Table 2-24 the maximum velocity is 0.26 m/day. In the subsequent dilution and attenuation calculations, the minimum (10 years), mean (34 years), and maximum (92 years) travel time will be used as key parameters.

Travel time class #	Travel time	"Top" particle release approach Proximity (CSG well– receptor) (km)	"Bottom" particle release approach Proximity (CSG well– receptor) (km)	Particle velocity (m/day)
1	<i>t</i> < 100 year	n: 20	n: 6	Mean: 0.12
	Mean: 33.8	Mean: 1.36	Mean: 1.72	Min: 0.03
	Min: 10.0	Min: 0.5	Stdev: 1.05	Max: 0.26
	Max: 91.7	Max: 3.4		Stdev: 0.04
	Stdev: 26.6	Stdev: 1.01		
2	100 < <i>t</i> < 1,000 year	n: 4	n: 6	Mean: 0.054
		Mean: 2.78	Mean: 2.00	Min: 0.04
		Stdev: 0.687	Stdev: 0.79	Max: 0.06
				Stdev: 0.01
3	1000 < <i>t</i> < 10,000	n: 0	n: 15	Mean: N/A
	year	Mean: N/A	Mean: 5.66	Min: N/A
		Stdev: N/A	Stdev: 1.86	Max: N/A
				Stdev: N/A
4	10,000 < <i>t</i> < 100,000	n: 0	n: 7	Mean: N/A
	year	Mean: N/A	Mean: 7.54	Min: N/A
		Stdev: N/A	Stdev: 3.22	Max: N/A
				Stdev: N/A

Table 2-24 Backward particle tracking travel time classes and corresponding proximity statistics for particles released at receptor locations located within a 30 km radius of the study area and tracked backward (i.e. upgradient) to locations within the study area. Data representative for Pilliga Sandstone.

2.6.5. Particle tracking analysis for the Surat Basin

The Dawson River in the northern part of the Surat Basin, Queensland (Figure 2-64), was selected as second test case area to undertake particle tracking analyses. The reasoning for selecting this area is as follows:

- There are many significant Great Artesian Basin (GAB) springs in this area, for which comprehensive conceptual models have been developed by QWC (2012) and OGIA (2016). Other CSG areas, such as the Condamine River area, have no mapped GAB springs;
- This area is of great interest to many stakeholders, particularly due to the on-going conceptual uncertainties on groundwater flow directions in the key aquifers such as the Hutton Sandstone. There has been considerable research done on this area as part of the first phase of GISERA (Suckow et al. 2016). This area is also the focus of the continuation of GISERA-funded research in Queensland.
- There is a significant alluvial aquifer system of the Dawson River within this area. In comparison to the Condamine River alluvium, this alluvial aquifer system is much thinner and not as wide. The Dawson River has cut into the Walloon Coal Measures (in Figure 2-64 these form a part of the Injune Creek Group) and other sedimentary bedrock units, and there may be a close connection between alluvium, surface water and the Walloon Coal Measures.



Figure 2-64 Selected case study area for the Surat Basin. See Figure 2-65 for cross-section.

2.6.5.1. Hydrogeology

The Queensland Water Commission (now known as Office of Groundwater Impact Assessment, OGIA) commissioned GHD to develop a groundwater model in 2012 (GHD 2012) to predict the cumulative groundwater impacts of Coal Seam Gas development in the Surat Cumulative Management Area. The predictive modelling using this model informed identification of immediately affected areas and long-term affected areas in Queensland Government's Underground Water Impact Report (QWC 2012). This groundwater model is used in the present study to undertake particle tracking analysis. At the time when this analysis was undertaken an updated groundwater model and impact assessments was being prepared by OGIA; this model was not available at the time the particle tracking analysis were undertaken.

In this model, the model layers represent either a single geological unit (e.g., Gubburamanda Sandstone) or a combination of multiple units (e.g., layer 3) (Table 2-25). Before the numerical discretisation of the geological layers (column 2) was undertaken, further aggregation or disaggregation was applied (column 1 in Table 2-20). For example, the Walloon Coal Measures is represented as 2 layers in the numerical model.

For the purpose of particle tracking analysis, the main hydrostratigraphic unit of interests are the Walloon Coal Measures and the sandstone aquifers above the Walloon Coal Measures - the Gubburamanda Sandstone and Springbok Sandstone. As the representation of the Alluvium in this model is very coarse, particle tracking analysis is not explicitly done for this layer.



Table 2-25 Summary of geological units, hydrostratigraphic units and groundwater flow model layers represented in Office of Groundwater Impact Assessment (OGIA) flow model (GHD 2012).

The Surat Basin comprises sequences of alternating layers of sandstones, siltstones and mudstones. The sandstone aquifers in the basin are the Mooga Sandstone, Springbok Sandstone, Hutton Sandstone and the Precipice Sandstone. The

fine to medium-grained, often clayey sandstones, siltstones and mudstones of the Springbok Sandstone overlie the Walloon Coal Measures.

Outcrop of different formations is as represented in the OGIA model (GHD 2012). All the formations outcrop along the north-eastern margin of the Surat Basin. A cross-section through the northern part of the Surat Basin highlights spatial relationships between different formations (Figure 2-65). In this northern part of the Surat Basin (Mimosa Syncline), the Dawson River has cut into the underlying bedrock. Although one would intuitively assume that groundwater flows from the northern outcrop beds to the central deeper parts of the Surat Basin, a recent study by Hodkinson and Grigorescu (2011) indicates that groundwater flow in key aquifers such as the Hutton Sandstone is towards the north in this area.



Figure 2-65 Cross-section through the northern part of the Surat Basin showing aquifer-aquitard sequence. For location of cross-section, see Figure 2-64.

Although geological formations are often represented as a single layer for modelling purposes, there is generally a high degree of lithological heterogeneity within most formations. Within the Walloon Coal Measures, for instance, there are alternating sequences of sandstone, siltstone, mudstone, carbonate shale and clay, and only a comparatively small proportion of the overall thickness is coal, as highlighted in Figure 2-67 and Figure 2-68. The coal seams are generally the more-permeable units that sit within a sequence of mainly low-permeability mudstones, siltstones or fine-grained sandstones. As shown in Figure 2-67, most of the coal seams comprise multiple thin lenses separated by layers of low-permeability sediments. The coal thickness typically makes up less than 10 per cent of the total thickness of the Walloon Coal Measures.



Figure 2-66 Lithological variability within the Walloon Coal Measures (OGIA 2016).



Figure 2-67 Example of lithological composition in Westbourne Formation, Springbok Sandstone and Walloon Coal Measures (herein represented by Durabilla Formation, Taroom Coal Measures, Tangalooma Sandstone and Juandah Coal Measures) in selected Surat Basin wells (Esterle et al. 2013)

2.6.5.2. Groundwater flow model

The OGIA groundwater model (GHD 2012) is a regional-scale numerical groundwater flow model of the Surat and Bowen Basins. This model was developed for quantifying the groundwater Impacts of CSG development within the Surat Cumulative Management Area (CMA). The major CSG proponents within the CMA are APLNG, QGC, Santos and Arrow Energy. The CSG development by all these proponents target the coal seams within the Walloon Coal Measures. The groundwater model was used by Queensland Water Commission to identify the immediately affected areas and long-term affected areas. Simulations of water extraction from the coal seams provided regional-scale predictions of depressurisation and drawdown of hydraulic head within the Surat and Bowen Basins and the associated induced flows between groundwater sources and hydrostratigraphic units. The same model has been used in this study for the particle tracking analysis. Porosity values used are in the range 0.1 to 0.25, with a constant value per model layer (guestimated from a porostiy - perm relationship that was reported for Precipice Sandstone (Janardhanan and Moore 2015).

The groundwater model is a MODFLOW 2005 model, and comprises 441 rows by 365 columns. For groundwater flow simulations, the geological domain was discretised using a combination of 1.5 km² cells leading to up a maximum of 160,965 model cells in one layer. Vertically, the model is discretized into 19 layers (Table 2-25). Coal seam gas production was simulated using the MODFLOW EVT package of the MODFLOW 2005 model. While the EVT package is normally used for calculating evapotranspiration, the OGIA model imposed water flux boundary conditions reflecting water abstraction through CSG wells by implementing the EVT package.

Groundwater abstraction is implemented in the model explicitly using the MODFLOW well package. Diffuse recharge was implemented using the MODFLOW recharge package. Surface water – groundwater interaction within the modelled area is simulated using the MODFLOW Drain and River packages. The surface water courses are represented in such a way to act as discharge boundaries only in this model, and thus surface water bodies water cannot recharge into the groundwater system. The local scale effects of these assumptions and their impact on the flow system may impact the particle tracking. However, tracking of particles from the deeper model layers will not be largely affected by these approximations.

The sinks for particles in the OGIA model are:

- river package and drain package cells representing rivers and other discharge boundaries,
- Well Package cells.

2.6.5.3. Forward particle tracking analysis

CSG wells in the Combabula North, Combabula and Reedy Creek tenements were chosen for the preliminary particle tracking analysis. A 144×112 km² area around these tenements was chosen for the preliminary particle tracking analysis. The bounding coordinates of the chosen buffer area are (675449, 7052087) and (819534, 7164557) in Australia GDA94 Z55 (Geocentric Datum of Australia units). A 30-km buffer area was used in this study for limiting the spatial analysis to an area large enough to capture all pathways identified through particle tracking analysis.

2.6.5.3.1. Baseline case without hydraulic fracturing

Consistent with Section 2.6.4.3.2 for the study area in New South Wales, the baseline case for the Surat explores whether any naturally occurring flowpaths exist between the main coal formations (i.e. Walloon Coal Measures) and the overlying aquifers. The analysis involves releasing particles within the Walloon Coal Measures layer and tracking their pathway until their final position. This calculation assumes there are no hydraulic fracturing induced pathways between the coal layers and the aquifers.

To test whether the buffer area was sufficiently inclusive of all pathways, a preliminary particle tracking analysis was undertaken by releasing particles from 362 CSG well locations within the Combabula North, Combabula and Reedy Creek tenements (Figure 2-69). During these calculations pumping from CSG wells is disabled. Based on these calculations, all the particles' travel distance over a period of 100,000 years are within the 30-km buffer zone (not shown).



Figure 2-68 Selected CSG wells and an overlay of the flow model grid. Particle tracks from particles released in the Walloon Coal Measures.

2.6.5.3.2. Hydraulic fracturing induced pathways

Subsequently particle tracking analyses are undertaken under the assumption that due to hydraulic fracturing additional pathways have been generated that connect the hydraulically stimulated coal formations with overlying aquifers. To better understand the connectivity between the key aquifer formations – the Gubberamunda Sandstone, the Springbok Sandstone, and the Hutton Sandstone – and the Walloon Coal Measures, which is the primary coal seam gas target formation, particles are now released in these aquifers.

The 362 CSG well locations were inputted into the groundwater model. The ADV2 package of MODLFOW was used for simulating the particle tracks (Anderman and Hill 2001). Advective transport of particles in the forward direction was simulated by releasing particles in each model cell containing the CSG wells. This forward analysis has its particle source at the well locations and the particles are tracked for a simulation time period of up to 100,000 years. For the three different simulations (one for each aquifer), the source of the particles was considered to be in the model cell at the bottom of the formation. The resulting particle tracks for each formation are shown in Figure 2-70 for the Gubberamunda Formation, Figure 2-71 for the Springbok Sandstone, and Figure 2-72 for the Hutton Sandstone.



Figure 2-69 Plan view of the particle tracks originating from the Gubberamunda formation.



Figure 2-70 Plan view of the particle tracks originating from the Springbok Sandstone aquifer.

The preliminary analysis indicated that particles released in the Gubberamunda Formation tend to travel towards the Springbok Sandstone formations that is underlying the Gubberamunda. Near the chosen tenements the Gubberamunda Sandstone is outcropping. Similarly, the particles released in the Springbok Sandstone travels towards the Walloon Coal Measures underlying the Springbok Sandstone. However, the majority of the particles released in the Walloon Coal Measures travelled only within the same formation. This is primarily because in the flow model the Walloon Coal Measures are conceptualised using three numerical model layers (layers 9, 10 and 11) where the layers 9 and 11 were conceptualised as aquitards. The particles that were released into the layer 10 never exited that layer within 100,000 years run time.



Figure 2-71 Plan view of the particle tracks originating from the Hutton Sandstone.



Figure 2-72 Distributions of particle travel distance.

Particles, in general, travelled larger distances in the aquifer formations compared to the Walloon Coal Measures (Figure 2-73). Among the sandstone formations, the particles released in the Hutton Sandstone tended to travel towards the north along uniform flow paths; these particles travelled the longest distances among all aquifers, indicating higher flow velocities in this particular aquifer. Particles travelled shorter distances in the Springbok Sandstone reflecting low hydraulic conductivities of this formation.



Figure 2-73 Distribution of particle travel times.

Distribution of travel times for the Gubberamunda Sandstone and Hutton Sandstone varied over a smaller range compared to the Springbok Sandstone and the Walloon Coal Measures (Figure 2-74). Walloon Coal Measures and Springbok Sandstone, on the other hand showed a wide range of travel times indicative of more complex travel paths and more variable aquifer hydraulic properties. The statistics of travel time and distances for the forward particle tracking analysis are shown in Table 2-26.

Table 2-26 Statistics of travel times and distances fr	from the forward particle	tracking analysis for the Surat Basin
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Release formation	Travel time statistics (years)	Travel distance statistics (km)
	Min: 0	Min: 0
Cuble are reasoned a Canadatana	Max: 105,326	Max: 39
Gubberamunua Sandstone	Mean: 46,411	Mean: 14
	Stdev: 34,686	Stdev: 12
	Min: 0	Min: 0
Covingbal Conditions	Max: 1,421,397	Max: 33
Springbok Sandstone	Mean: 478,349	Mean: 10
	Stdev: 316,078	Stdev: 6
	Min: 0	Min: 0
Walloon Coal Measures	Max: 4,615,268	Max: 69
Walloon Coal Measures	Mean: 994,938	Mean: 11
	Stdev: 1,082,862	Stdev: 10
	Min: 0	Min: 0
Hutton Sandstone	Max: 280,092	Max: 69
	Mean: 128,192	Mean: 33
	Stdev: 62,086	Stdev: 11

2.6.5.4. Backward particle tracking analysis

Backward particle tracking analysis was undertaken to analyse the travel distances and travel times for particles reaching specified receptor bore locations in the Gubberamunda Sandstone. A total of 119 pumping water bores in the Gubberamunda Sandstone that are within and around the CSG well field were chosen for backward particle tracking analysis. In order to avoid the pumping water bores acting as sinks and resulting in the immediate exit of the particles through these sinks, simulation of pumping water bores was turned off in the backward particle tracking analysis.



Figure 2-74 Backward particle tracks for particles released within the Gubberamunda Sandstone.

The Gubburamanda Sandstone outcrops in the region where the CSG wells are present. It was found that the particles from the receptor bores located towards the west of the CSG well field track backwards in the northwest direction and the majority of the particles from receptor bores located towards the east of the CSG well field tracked back in the south west direction. Contours of the modelled heads for the Gubburamanda Sandstone are also shown Figure 2-75.

The distributions of particle travel distances and times from the backward particle tracking for Gubburamanda Sandstone are shown in Figure 2-76 and the relevant statistics are summarised in Table 2-27. Whenever particles have a zero travel distance the particle has not moved from its starting position (i.e. the water bore).



Figure 2-75 Distribution of travel times for the backward particle tracking analysis.

Travel time class #	Travel time	Particle travel distance (km)	Particle velocity (m/day)
1	<i>t</i> < 100 year	Mean: 0.00	Mean: 0
		Min: 0.0	Min: 0
		Max: 0.0	Max: 0
		Stdev: 0.00	Stdev: 0
2	100 < <i>t</i> < 1,000 year	Mean: 0.09	Mean: 6.13E-04
		Stdev: 0.08	Min: 6.08E-05
			Max: 1.19E-03
			Stdev: 4.89E-04
3	1000 < <i>t</i> < 10,000 year	Mean: 0.87	Mean: 8.57E-04
		Stdev: 1.25	Min: 1.77E-04
			Max: 2.14E-03
			Stdev: 5.83E-04
4	10,000 < <i>t</i> < 100,000 year	Mean: 3.70	Mean: 3.71E-04
		Stdev: 1.80	Min: 3.86E-06
			Max: 7.91E-04
			Stdev: 1.69E-04

Table 2-27 Travel time and distance statistics for the backward particle tracking for particles released in the Gubberamunda Sandstone.

A second backward tracking analysis was undertaken by considering only receptors (i.e. water bores) within the Walloon Coal Measures. Particles were released within the Walloon Coal Measures at the location of the water bores and their pathway recorded. As is evident from Figure 2-77, none of the pathlines is connect with any of the CSG wells. In other words, the CSG wells are hydraulically disconnected from the water bores such that it becomes very unlikely that any chemicals potentially released from the CSG wells will flow into these water bores. Furthermore, the groundwater velocity is very small; based on the particle travel time and distance output, the statistics of the pore-water velocity are as follows: minimum = 9.5×10^{-5} m/d, mean = 4.6×10^{-4} m/d, maximum = 5.4×10^{-3} m/d and standard deviation = 9.4×10^{-4} m/d. the mean velocity of 4.6×10^{-4} m/d falls within the range of mean values derived for the Gubberamunda aquifer (i.e. from 6.13×10^{-4} m/d – 3.71×10^{-4} m/d) (Table 2-27).



Figure 2-76 Backward particle tracks for particles released within the Walloon Coal Measures. Receptors represent water bores.

3. Spatial analyses of CSG extraction activities, hydraulic fracturing operations, and relevant assets

The hazard screening methodology requires information on linear distance from coal seam gas extraction activities (the potential contaminant source in deeper groundwater) to relevant assets (water bores for bulk and municipal drinking water off-takes, surface water assets such as springs, streams, wetlands, and sites of historical or cultural significance) in order to assign a likelihood class to a chemical-specific DAF. In this way the DAFs can be interpreted in a spatial risk framework, i.e. while the DAF itself is a measure of consequence (dividing a source concentration by a DAF results in a predicted environmental concentration), the spatial analysis assigns a probability to each DAF by which the initial hazard screening (and hazard ranking based on a chemical's DAF) becomes extended to a risk screening.

3.1. Methodology

The approach is based on a similar spatial analysis undertaken for the Namoi alluvial as part of the National CSG Chemicals Assessment Project – Phase 1 (Mallants et al. 2017a). This analysis resulted in region-specific frequency-proximity¹³ relationships that quantified the probability of encountering a water bore within 1 km from a CSG well (see Figure 3-1 for a theoretical example). Further, Figure 3-1 depicts the methods for linking DAF classes to a probability values or classes.

Similar frequency-proximity relationships were determined for aquatic ecosystems (Mallants et al. 2017a). In addition to being a key element of assigning probabilities to DAF values, the frequency-proximity relationships may also be used to derive a setback distance for any of the receptors, e.g. water bores, beyond which impacts can be demonstrated to be negligible.

It was previously determined by CDM Smith (2014) that any potential depressurisation relating to CSG operations would not extend beyond 30 km of any CSG well. Therefore, the proximity analysis was constrained to within this distance in the current study. The proximity analysis was constrained according to angle from CGS wells. For the Gunnedah Basin, particle tracking analysis revealed travel from CSG wells was expected to be in a generally northerly direction but ranging from east to west (Figure 2-54). The proximity analysis was therefore conducted on elements located within angles from 270° (due west) through to 90° (due east) degrees (either to north or south depending if analysis was from CSG well to receptor – forward tracking – or visa versa – backward tracking). In other words, proximities will be calculated in the direction of the main groundwater flow; no proximities will be calculated in the direction opposite to groundwater flow. A similar approach was adopted for the Surat Basin.

Contaminant source-asset frequency-proximity relationships were determined using the geographical information systems (GIS) ArcGIS[™] and relevant databases with key assets (where data is accessible for this project). The study areas involved are a subset of the Surat Cumulative Management Area (CMA) covered by OGIA's groundwater model and an area in the Gunnedah Basin near Narrabri, NSW, covered by the CDM Smith (2014) groundwater model.

The methodology for linking frequency-proximity relationships with DAF is summarised in Figure 3-1. It involves the following steps:

 Determine proximity (linear distance) – frequency (probability of non-exceedance) relationship based on distance between coal seam gas wells and assets (within a distance of 30 km from any coal seam gas well). Note

¹³ Proximity = set of shortest straight lines among all points

this probability expresses purely the likelihood of encountering a certain asset within a given distance from a CSG well; effects of CSG operations (e.g. whether the well is fractured or not) are not considered,

- Calculate travel time from coal seam gas wells to assets that have a demonstrated connection via groundwater using solute particle tracking analysis. Because several pathlines originating from multiple coal seam gas wells can end in one and the same asset, a travel time probability density function is derived for each asset.
- Aggregate travel times in classes as a means to summarise the travel time data, e.g. from 1-5 years, 5-10 years, 10-50 years, etc. Each class is characterised in terms of a probability density function with its mean, standard deviation, and percentiles.
- Calculate chemical-specific DAFs by using travel time to calculate biological/chemical attenuation (transformation/degradation) linked with geological attenuation (sorption)
- Define likelihood for DAF classes by linking travel time class to its respective linear distance-frequency.



Figure 3-1 Methodology for linking DAF classes to probability (likelihood). Top panel shows for a set of CSG wells and water bores i) frequency distribution of CSG well – bore distances based on spatial analysis and ii) frequency distribution of CSG well – bore travel times based on particle tracking analysis. Middle panel shows cumulative frequency of CSG well – bore distances and table with travel time characteristics (mean and standard deviation for travel time distribution) for water bores. Bottom panel shows calculated dilution attenuation factors (DAF) for a given chemical. DAF values are assigned a likelihood based on the travel distance – probability curve.

Three analytical methods for determining the distribution of proximity relationships were tested in order of complexity and computational demand:

- 1. Distribution of proximities of asset features to the nearest coal seam gas well for each asset group, subgroup and class:
 - identify the distance between any *N* assets (for each asset class) and the nearest (and only nearest) coal seam gas well within a radius of 30 km from each asset feature, resulting in *N* nearest distances (*N* is the sample size of the data set),
 - exclude records of distances to coal seam gas wells located north of assets (and hence not in a potential pathway with the asset based on the particle tracking analysis),
 - rank the N nearest distances from smallest to largest,
 - assign a rank number (i) to each of the N distances, from 1 for the smallest to N for the largest distance,
 - calculate the cumulative empirical probability (or cumulative distribution function cdf) *i*/*N*, or the probability that the distance is less than or equal to the value associated with distance *i*. In doing so the largest observation will have a cumulative probability *i*/*N* = 1, and therefore has a (theoretical) zero probability of being exceeded. To allow for a non-zero probability of exceeding the largest value observed in a sample, so-called plotting positions are used, rather than using *i*/*N*. Here the Weibull plotting position formula was applied (probability = *i*/*N*+1) rather than *i*/*N*. The Weibull formula has long been used by hydrologists in the United States for plotting flow duration and flood-frequency curves (Helsel and Hirsch 2002). In doing so, the empirical cumulative distribution function will more closely mimic the underlying population cumulative distribution function.
- 2. Distribution of proximities of asset features to the nearest 5 coal seam gas wells for each asset group, subgroup and class:
 - identify the distances between any *N* assets (for each asset class) and the nearest 5 coal seam gas wells within a radius of 30 km from each asset feature,
 - exclude records of distances to coal seam gas wells located north of assets (and hence not in a potential pathway with the asset based on the particle tracking analysis),
 - rank the N nearest distances from smallest to largest,
 - assign a rank number (i) to each of the N distances, from 1 to the smallest to N for the largest distance,
 - apply Weibull plotting position formula (probability = *i*/*N*+1) and calculate cumulative distribution function.
- 3. Distribution of proximities of each (424 in case of the Gunnedah Basin) coal seam gas well pairs to all asset features for each asset group, subgroup and class:
 - identify the distances between all coal seam well pairs (N = 424) and any N assets (for each asset class) within a radius of 30 km from each asset feature,
 - exclude records of distances to assets located south of coal seam gas wells (and hence not in potential pathway with the asset based on the particle tracking analysis),
 - rank the N nearest distances from smallest to largest,
 - assign a rank number (i) to each of the N distances, from 1 to the smallest to N for the largest distance,
 - apply Weibull plotting position formula (probability = *i*/*N*+1) and calculate the cumulative distribution function.

Note that in the first approach only the distance to the nearest coal seam gas well is accounted for, and therefore uses only a (relatively small) subset of all possible distances (a total of 1*N distances is considered). For example, in the case of the Gunnedah Basin, 424 coal seam gas wells are considered in the spatial analysis. As a result of this method, the subset for

any asset class represents a 1/424 fraction of all possible distances. In the second approach the theoretical maximum number of distances is 5*N. For the practical case of the Gunnedah Basin, the number of distances recorded was less than 5*N as distances to any of the nearest 5 coal seam gas wells located north of assets were filtered out. The third method considers all possible distances and was therefore selected here for the spatial analysis; the first and second method severely underestimate the number of connections which may introduce bias in the data set. For the same reason as for the second method, the number of distances recorded for the third approach was less than the theoretical maximum 424*N.

For spatial analyses the GIS shape type of the elements in the Asset Register was an important consideration. Within the Namoi Asset Register geodatabase, point, line and polygon feature types were stored as multipart features, i.e. unique features comprised one or more parts (spatial units). The proximity analysis measures the distance from the source feature (in this case the CSG wells) to the nearest part of unique target features (in this case elements) thus disregarding any other spatially discrete parts of a multipart feature. It was considered important to account for distances to discrete features of elements (i.e. features occurring at more than one location). Multipart features were therefore converted or disaggregated to singlepart features so that distances to each element or element part would be measured and included in the frequency-proximity analysis. This conversion preserves the attributes of the input features while each individual feature part is assigned a new object identifier and becomes a discrete spatial unit (Figure 3-2 and Figure 3-3). The method used to split multipart features does not necessarily rely on spatial separation, as elements of multipart features can overlap, intersect and share boundaries. The split occurs only on multipart features; features that are already singlepart will not be affected. Singlepart features, by definition, are a single discrete spatial object part (point, line segment or enclosed polygon). Disaggregation of features in the Namoi Asset List database (Version 5) resulted in 10 multipart line features becoming 119 singlepart features, 2,074 multipart polygon features becoming 12,862 singlepart features, and 89 multipart point features becoming 8,894 singlepart features.



Figure 3-2 Schematic representation of multipart and singlepart features in ArcGIS (from ArcGIS Resource Centre).



Figure 3-3 Multipart and singlepart line feature representation; line segment representing a single line feature highlighted in singlepart panel is part of one multipart line feature shown highlighted in the multipart panel.

The proximity – frequency relationship can also be used for hypothesis testing, in that a test can be performed on whether the possibility of a hypothesised impact occurring can be rejected with a high probability. For instance, a typical hypothesis could be one that considers contamination of a domestic bore 500 m from the coal seam gas well. Hypothesis testing enables the rejection of the possibility of such an occurrence with high probabilities such as 95 or 99%.

3.2. Frequency-proximity relationships for Gunnedah Basin

3.2.1. Ecological assets

3.2.1.1. Groundwater dependent ecosystem asset class

Cumulative probability plots of horizontal distance of assets from CSG wells for the GDE asset class determined through the three approaches are shown in Figure 3-4 to Figure 3-6. Distances of zero m (i.e. features – primarily large polygons that occur throughout the study area, see Figure 2-18 - directly interesting with CSG well locations) are not shown on the log₁₀ scale plots, however, their distributional parameters are accounted for. As a result, the probability associated with the first non-zero distance is often relatively large, e.g. several percentages. This explains why the cumulative probability curve deviates from a more or less straight line.

Assets directly intersecting CSG wells included groundwater dependent vegetation features (mainly native vegetation) and other undefined ecosystems (GDE1 and GDE5) in the Asset Register (see Figure 2-18). The River GDE on Bohena Creek was found at ~2m and Eather Spring and Hardys Spring GDEs were found at ~2.5km.



Figure 3-4 Cumulative probability of the proximity of the nearest CSG well (in m) to assets (Approach #1) in the Groundwater Dependent Ecosystems Class (Ecological Assets, Vegetation Subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells.

The cumulative probability distribution based on Approach #1 and #2 is highly affected in the lower percentiles where less observations (distances) are included resulting in over-estimation of the probability when compared to Approach #3 (Figure 3-6). The overall shapes of the distribution curves are similar across methods, however especially the short-distance proximities become much more accurate. Also, the influence of zero distance values is reduced through the inclusion of more observation with non-zero values in Approach #3 (and to a lesser extent Approach #2). Although all probabilities decrease when more data points are added to the sample, the largest effect is noticed for smallest probabilities. Because Approach #3 provides a more accurate description of the frequency-proximity relationship at shorter distance, which is the most critical distance in terms of risk, Approach #3 was used throughout all further analyses.



Figure 3-5 Cumulative probability of the proximity of up to 5 of the nearest CSG wells to assets (Approach #2) in the Groundwater Dependent Ecosystems Class (Ecological Assets, Vegetation Subgroup) within a distance of 30 km and an angle south between 90°E and 270°W from assets.



Figure 3-6 Cumulative probability of the proximity of all CSG wells to assets (Approach #3) in the Groundwater Dependent Ecosystems Class (Ecological Assets, Vegetation Subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells.

3.2.1.2. Aquifer, geological feature, alluvium or stratum asset class

The cumulative probability distribution of proximities of assets in the aquifer, geological feature, alluvium or stratum Class (Ecological Assets, groundwater feature subgroup) from CSG wells are shown in Figure 3-7. Several assets directly intersected proposed CSG wells; these included Cadna-Owie Hooray Equivalent Gab Recharge, Great Artesian Basin Groundwater Management Zone, Narrabri Water Table Aquifer, and Westbourne Formation. These assets accounted for >40% of all distances recorded between CSG wells and asset features in this Class. This explains why the cumulative distribution for the first proximity asset at 6 m has a value of just over 40%; indeed, all the zero-distance assets account for 40%. These assets were also the only ones found within ~2.5 km, while beyond this distance the Gunnedah Basin Groundwater Management Zone and Upper Namoi Alluvium were found at ~7 km. Riverine Plain Alluvium and Tertiary Volcanics assets were found at distances >28 km from CSG wells.



Figure 3-7 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Aquifer, geological feature, alluvium or stratum Class (Ecological Assets, groundwater feature subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells.

3.2.1.3. Habitat (Potential Species Distribution) asset class

Cumulative probability distribution of distances of assets in the Habitat (Potential Species Distribution) asset class from CSG wells are shown in Figure 3-8. A number of these directly intersected CSG well locations. These included *Philotheca ericifolia*, Brigalow Park Nature Reserve, Cattle Egret (*Ardea ibis*), Coolibah - Black Box Woodlands Of The Darling Riverine Plains And The Brigalow Belt South Bioregions, Great Egret, White Egret (*Ardea spp.*), Koala (*Phascolarctos cinereus*), Pilliga important bird area (IBA), Potential Distribution Of South-Eastern Long-Eared Bat (*Nyctophilus corbeni*), Regent Honeyeater (*Anthochaera phrygia*), Spiny Pepper-Cress (*Lepidium aschersonii*), White-Bellied Sea-Eagle (*Haliaeetus leucogaster*). These zero-distance assets accounted for ~11% of all distances observed. The Natural Grasslands on Basalt And Fine-Textured Alluvial Plains of Northern New South Wales and Southern Queensland were found at ~3 km and the potential habitat of the Australian Painted Snipe (*Rostratula australis*) was found at ~4 km. Remaining assets in this class were >11 km from CSG wells and comprised mainly of conservation areas, woodlands, flora reserves and National parks.



Figure 3-8 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Habitat (Potential Species Distribution) Class (Ecological Assets, Vegetation subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells.

3.2.1.4. Surface water feature asset subgroup

The cumulative probability distribution of distances of assets in the surface water feature asset subgroup from CSG wells are shown in Figure 3-9. This subgroup includes the following asset classes: river or stream reach, tributary, anabranch or bend; floodplain; wetland, wetland complex or swamp; lake, reservoir, lagoon or estuary; marsh, sedgeland, bog, spring or soak. A number of these directly intersected CSG well locations and included local catchments for the Bibblewindi, Bohena, Bullock, Cowallah, Eulah, Killen Mount Pleasant, Sandy, Sawpit, Womera, and Yellow Spring Creeks. Also intersected were the Reedy Gully, Bohena, Brigalow, and Bundock sub-catchments, the Bundock Floodplain, Cowallah Creek and the EEC on the Namoi-Gwydir River. At distances of 8 to 230 m, Sawpit, Pine, Mount Pleasant, Yellow Spring, Mollee, Jacks, Bundock, Bibblewindi, Sandy, Bohena and Killen Creeks are intersected. From 230 m to 1 km (800 m), Tributary of Bibblewindi Creek, Dead Bullock and Tuppiari Creeks, Other Wetland 166 and Reedy Gully were intersected.



Figure 3-9 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the River or stream reach, tributary, anabranch or bend; Floodplain; Wetland, wetland complex or swamp; Lake, reservoir, lagoon or estuary; Marsh, sedgeland, bog, spring or soak Classes (Ecological Assets, Surface Water Feature subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells.

3.2.2. Economic assets

3.2.2.1. Groundwater management zone subgroup

Cumulative probability distribution of distances of assets in the Water Access Right class (economic group, groundwater management zone subgroup) from CSG wells are shown in Figure 3-10. Within a distance of 1 km (and up to ~8.3km) all assets were named 'Water Access Right Southern Recharge Groundwater Source'. These assets include groundwater bores for purposes including aquaculture, domestic, stock, farming, industrial, firefighting, mineral water extraction, irrigation, and recreation; and the Water Access Right in Upper Zone 4, Namoi Valley (Keepit Dam To Gin'S Leap) Groundwater Source area.



Figure 3-10 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Water Access Right Class (Economic Assets, Groundwater management zone subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells. Assets include groundwater bores for purposes including aquaculture, domestic, stock, farming, industrial, fire fighting, mineral water extraction, irrigation, and recreation; and the Water Access Right In Upper Zone 4, Namoi Valley (Keepit Dam To Gin's Leap) Groundwater Source area.

Cumulative probability distribution of distances of assets in the Basic Water Right class (economic group, groundwater management zone subgroup) from CSG wells are shown in Figure 3-11. Assets include groundwater bores for purposes including water conservation, domestic, stock, teaching and 'unknown'; and Groundwater Management Plan areas for the Upper and Lower Namoi sources, NSW GAB, and the NSW MDB Fractured and NSW MDB Porous Rock sources. The latter 3 plan areas intersect directly with proposed CSG well locations. From ~50m bores within the Basic Access Right Southern Recharge Groundwater Source were located. Bores within the Basic Access Right Gunnedah-Oxley Basin MDB Groundwater Source were located from ~4 km from CSG wells. Bores in the Lower Namoi and Upper Namoi Zone 5 Namoi Valley (Gins Leap to Narrabri) Groundwater Source were located from ~7 km and ~7.5 km from CSG wells respectively. Bores within the Upper Namoi Zone 11 Maules Creek Groundwater Source were located from ~18 km from CSG wells.



Figure 3-11 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Basic Water Right (stock and domestic) Class (Economic Assets, Groundwater management zone subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells. Assets include groundwater bores for purposes including water conservation, domestic, stock, teaching and 'unknown'; and Groundwater Management Plan areas for the Upper and Lower Namoi sources, NSW GAB, and the NSW MDB Fractured and NSW MDB Porous Rock sources (the latter 3 intersect directly with the proposed CSG wells).

3.2.2.2. Surface water management zone subgroup

Cumulative probability distribution of distances of assets in the Water Access Right class (economic group, surface water management zone subgroup) from CSG wells are shown in Figure 3-12. Assets located from ~900 m include water sources for Bohena and Eulah Creeks. From ~9 km water access right Lower Namoi Regulated River Water source were located and from ~17km to ~23km water access right locations for the Bundock, Maules, Brigalow and Pian Creek water sources were located. Purposes for this asset class include augmentation, domestic, irrigation, stock, farming, horticulture, industrial, mining, recreation, and recirculation and contained both low and high security water access rights.



Figure 3-12 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Water Access Right Class (Economic Assets, Surface water management zone subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells. Assets include Water Access Right locations for the Lower Namoi River and the Bohena, Brigalow, Bundock, Eulah, Spring, Bobbiwaa, Maules, Pian, and Millie Creeks.

Cumulative probability distribution of distances of assets in the Water Access Right class (Economic group, Surface water management zone subgroup) from CSG wells are shown in Figure 3-13. This asset class included source locations within water sharing plan areas. Four of these plan areas directly intersected the proposed CSG well locations, these were the Water Sharing Plan areas for the Namoi Unregulated and Alluvial Water Sources including Bohena Creek Water Source, Brigalow Creek Water Source, Bundock Creek Water Source, and the Eulah Creek Water Source. The Coghill Creek Water Source Water Sharing Plan area was located from ~2.7 km. From ~9 to ~29 km, water access right locations were located within Lower Namoi Regulated River Water Source, Spring and Bobbiwaa Creeks Water Source, Spring And Bobbiwaa Creeks Water Source, Maules Creek Water Source, Bluevale Water Source and the Pian and Millie Creeks Plan areas.



Figure 3-13 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Basic Water Right (stock and domestic) Class (Economic Assets, Surface water management zone subgroup) within a distance of 30 km and an angle north between 90°E and 270°W from CSG wells. Assets include Water Sharing Plan areas (management zones) for Basic Water Rights (stock and domestic) for the Lower Namoi River and the Bohena, Brigalow, Bundock, Eulah, Spring, Bobbiwaa, Maules, Pian, and Millie Creeks.

3.2.3. Sociocultural assets

Cumulative probability distribution of distances of assets in the sociocultural asset group from CSG wells are shown in Figure 3-14. These assets comprised heritage and indigenous site asset classes. One of the 8 heritage sites within the 30 km study area buffer area was excluded from proximity analysis due to its position south of the proposed CSG wells (Figure 2-22). The remaining 7 hertitage sites and 1 indigenous site were >13 km from the nearest CSG well location (Figure 3-14). The Collins Park Grandstand, Police Residence, Narrabri Gaol (former), Narrabri Post Office and Former Telegraph Office and Narrabri Public School heritage sites were located 13.2 to 13.7 km from proposed CSG well locations. At distances of 23.8 to 26.9 km, the Bullawa Creek Area indigenous site and Wee Waa Courthouse and Mount Kaputar National Park hertitage sites were located.


Figure 3-14 Cumulative probability of the proximity of all assets to each CSG well pair (Approach #3) for assets in the Sociocultural Assets (cultural subgroup). Assets include heritage and indigenous sites asset classes.

3.3. Frequency-proximity relationships for the Surat Basin

3.3.1. Ecological assets

3.3.1.1. Surface Water Feature

The cumulative probability distribution of distances of assets in the Surface Water Feature asset subgroup from CSG wells is shown in Figure 3-15. This subgroup includes the following asset classes: river or stream reach, tributary, anabranch or bend; floodplain; wetland, wetland complex or swamp; lake, reservoir, lagoon or estuary; marsh, sedgeland, bog, spring or soak. The majority of these assets were stream systems and water courses and wetlands. A total of 36 assets were located within 1 km of CSG wells. These included various non-perennial water courses and creeks, and wetlands within the Dawson River catchment.



Figure 3-15 Cumulative probability of the proximity of assets to CSG wells for assets in the River or stream reach, tributary, anabranch or bend; floodplain; wetland, wetland complex or swamp; lake, reservoir, lagoon or estuary; marsh, sedgeland, bog, spring or soak Classes (Ecological Assets, Surface Water Feature Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

3.3.1.2. Groundwater Dependent Ecosystems asset class

The cumulative probability distribution of distances of assets in the GDE class of the Vegetation asset subgroup to CSG wells is shown in Figure 3-16. Within close proximity of CSG wells (e.g. <2 km), these GDEs mainly comprised native

vegetation areas (eucalypt woodlands and open forests, Acacia and Casuarina forests and woodlands). Other GDEs were identified as GDEs with high potential for groundwater interaction on certain water courses and creek lines e.g. Fitzroy River and Yuleba Creek.



Figure 3-16 Cumulative probability of the proximity of assets to CSG wells for assets in the Groundwater Dependent Ecosystems Class (Ecological Assets, Vegetation Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

3.3.1.3. Aquifer, geological feature, alluvium or stratum asset class

The cumulative probability distribution of distances of assets in the Aquifer, geological feature, alluvium or stratum class of the Groundwater Feature asset subgroup to CSG wells is shown in Figure 3-17. All nine assets within the 30 km search area directly intersected with CSG wells. Assets included Cadna-owie Hooray Equivalent GAB recharge area, Gubberamunda Sandstone, Hutton/Marburg and Evergreen Sandstone, Permian of the Bowen Basin, Precipice Sandstone, Springbrok Sandstone, Walloon Coal Measures, and Wandoan Formation.



Figure 3-17 Cumulative probability of the proximity of assets to CSG wells for assets in the Aquifer, geological feature, alluvium or stratum Class (Ecological Assets, Groundwater feature (subsurface) Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

3.3.1.4. Vegetation, Habitat Potential Species Distribution

The cumulative probability distribution of distances of assets in the Habitat Potential Species Distribution class of the Vegetation asset subgroup to CSG wells is shown in Figure 3-18. A number of assets (21) directly intersected with CSG wells and a further 7 were within 1 km of the wells. These included potential distribution of a various native animals (mainly birds) and vegetation (Acacia and Eucalypt species). Several threatened or endangered habitats intersected CSG wells, including the Acacia harpophylla and/or Casuarina cristata open forest on fine-grained sedimentary rocks Endangered Regional Ecosystem (as dominant component), Weeping Myall Woodlands Threatened Ecological Community, Brigalow (Acacia harpophylla dominant and co-dominant) Threatened Ecological Community, and the Semi-evergreen vine thickets of the Brigalow Belt (North and South) and Nandewar Bioregions Threatened Ecological Community. The Eucalyptus populnea, Acacia harpophylla open forest on fine-grained sedimentary rocks Endangered (as dominant component) and the Semi-evergreen vine thicket or Acacia harpophylla with a semi-evergreen vine thicket understorey on fine-grained sedimentary rocks Endangered Regional Ecosystem (as dominant component) habitats were located within 1 km of CSG wells. A detailed overview of habitat (potential species distribution) within the 30 km buffer zone is given in Appendix 4.



Figure 3-18 Cumulative probability of the proximity of assets to CSG wells for assets in the Habitat Potential Species Distribution Class (Ecological Assets, Vegetation Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

3.3.2. Economic assets

3.3.2.1. Groundwater management zone subgroup

The cumulative probability distribution of distances of assets in the Water Access Right class of the Groundwater Management Zone asset subgroup to CSG wells are shown in Figure 3-19. These assets included groundwater bores for purposes including aquaculture, domestic, stock, farming, industrial, firefighting, mineral water extraction, irrigation, and recreation. The closest asset to CSG wells (distance of 600 m) was the Water Access Right in Surat 4 Management Unit Subgroup Area. The rest were located between 17 and 30 km from CSG wells and included the Water Access Right in Surat 3 Management Unit Subgroup Area, Water Access Right in Roma Not Assigned Subgroup Area, Water Access Right in Surat North 2 Management Unit Subgroup Area, and Water Access Right in Surat North 3 Management Unit Subgroup Area.



Figure 3-19 Cumulative probability of the proximity of assets to CSG wells for assets in the Water Access Right Class (Economic Assets, Groundwater Management Zone Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

The cumulative probability distribution of distances of assets in the Basic Water Access Right (Stock and Domestic) class of the Groundwater Management Zone asset subgroup to CSG wells is shown in Figure 3-20. Assets included groundwater bores for purposes including water conservation, domestic, stock and 'unknown'. Within 1 km of CSG wells assets included bores within the BASIC RIGHT in Surat 4 Management Unit Subgroup Area, BASIC RIGHT in Surat 5 Management Unit Subgroup Area, and the BASIC RIGHT in Surat North 1 Management Unit Subgroup Area. From 1 to 10 km from CSG wells assets included bores within the BASIC RIGHT in Surat North 1 Management Unit Subgroup Area, BASIC RIGHT in Surat North 3 Management Unit Subgroup Area, BASIC RIGHT in Surat North 3 Management Unit Subgroup Area, and the BASIC RIGHT in Surat 7 Management Unit Subgroup Area, BASIC RIGHT in Roma Not Assigned Subgroup Area, and the BASIC RIGHT in Surat 2 Management Unit Subgroup Area. The remaining assets bores (4418 in total) were located >12 km from CSG wells.



Figure 3-20 Cumulative probability of the proximity of assets to CSG wells for assets in the Basic Water Right Class (Stock and Domestic) (Economic Assets, Groundwater Management Zone Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

3.3.2.2. Surface Water Management Zone, Water Access Right

The cumulative probability distribution of distances of assets in the Water Access Right class of the Surface Water Management Zone asset subgroup to CSG wells is shown in Figure 3-21. Purposes for this asset class include augmentation, domestic, irrigation, stock, farming, horticulture, industrial, mining, recreation, and recirculation and contained both low and high security water access rights. There was only one asset (Water access right Slatehill Creek water source) located 29 km from the nearest CSG well and was within the 30 km search distance to 9 CSG wells in total. Details about the type of bores encountered within 500 m of CSG wells is provided in Appendix 4.

There were no assets in the Basic Water Access Right (Stock and Domestic) class of the Surface Water Management Zone asset subgroup within the 30 km buffer zone around the maximum extent of particle tracking movement (see Table 2-13).



Figure 3-21 Cumulative probability of the proximity of assets to CSG wells for assets in the Water Access Right Class (Economic Assets, Surface Water Management Zone Subgroup) within a distance of 30 km and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

3.3.3. Sociocultural assets

There were no sociocultural assets located within 30 km of any CSG well. However, within the 30 km buffer zone around the maximum extent of particle tracking movement there were 2 assets (see Figure 3-22); Carraba Environmental Park-Roma Taroom Rd, Taroom (Recreation Area asset class) and Hornet Bank Homestead- Hornet Bank Rd, Taroom (Hertitage Site asset class). These assets were located 43 and 47 km respectively from the nearest CSG well.



Figure 3-22 Cumulative probability of the proximity of assets to CSG wells for assets in the Sociocultural asset group within the particle tracking buffer zone and an angle between 180°S and 90°E from CSG wells in the Surat Basin.

4. Chemical, biological and geological attenuation processes

Chemical/biological attenuation (chemical/biological degradation) and geological attenuation (adsorption) all contribute to natural attenuation. "Natural Attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biotransformation, dispersion, dilution, adsorption, volatilisation, and chemical or biological stabilisation or degradation of contaminants (US EPA 1998a).

In this section of the study, details are provided regarding the approach to integrate geological and chemical or (micro)biological attenuation processes into a single metric for attenuation of substances (Section 4.1). Transformation or degradation pathways and half-lives are identified as a means to ensure the analysis is sufficiently comprehensive, and accounts for both parent chemical compounds and their transformation products whose properties, including toxicity, may be quite different from their parents (Section 4.2). Next, information is collated on chemical mobility (retardation) for organic substances (Section 4.3) and inorganic substances (Section 4.4). The combination of sorption parameter and half-lives will improve understanding of attenuation processes and underpins determination remaining concentrations at the receptor for indicator chemicals. Toxicity of individual chemicals will also be compiled to complete the data collation process required for the hazard screening (Section 4.5).

4.1. Methodology

The hazard screening methodology uses information on chemical persistence (half-life) and mobility (retardation) to first determine the transport time from source to receptor from which subsequently the remaining concentration at the receptor location is determined (the travel time defines how much of the chemical will degrade to X% of the initial concentration). Chemical, microbiological, and geological attenuation processes relevant for deeper groundwater pathways have been reviewed (Section 4.2). Parameters for each of these processes have been collated from a literature review for characteristic chemicals (chemicals have been defined in Section 2.3). Chemical or microbiological degradation data has been sourced from groundwater attenuation studies in aerobic and anaerobic environments. Aerobic environments may be more appropriate for the transport pathways in unconfined and alluvial aquifers, while anaerobic transport pathways are more appropriate for the deeper confined aquifers and coal formations. If such data was not available, alternative methods have been used to estimate degradation rates using, e.g. the EPA BIOWIN-4 model.

In groundwater sediments, coal formations and interburden rocks, chemicals are temporarily removed from the water phase by an interaction with the solid matrix by chemical, physical or electrostatic forces. This process is generally called sorption (US EPA 1999b), and is referred-to here as geological attenuation. Two sorption phenomena are typically distinguished: adsorption/desorption and absorption. Adsorption refers to the processes in which the chemical accumulates on the surface of a solid particle (i.e. grains, organic matter). Desorption is the reverse of adsorption - chemicals are released from the solid particles back into the porewater. Absorption describes processes in which the contaminant becomes incorporated into the surface layer of a mineral structure.

Geological attenuation determines a chemical's mobility and requires estimation of the sorption or retention behaviour. The Freundlich equation or sorption isotherm is the simplest conceptualisation to quantify the behaviour of retention of reactive solutes with the soil or rock matrix. It has been used widely to describe solute retention by soils and aquifer sediments (Helfferich 1962; Sposito 1984; among others). The Freundlich equation is expressed as:

$$C_{ads} = K_d C_{liq}^b \tag{1}$$

where C_{ads} is the concentration of solute retained by the sediment in mg/g of dry sediment, C_{liq} is the solute concentration in solution in mg/ml, K_d is the solid-liquid partition coefficient in L/kg, and the parameter *b* is dimensionless and typically has a value of b < 1.

For b = 1, the (nonlinear) Freundlich equation reduces to a linear sorption equation. The K_d parameter then quantifies instantaneous, linear and reversible sorption, and depends on the type of porous medium and on the chemical element (Thibault et al. 1990). It describes the capacity of a solid to remove a dissolved chemical from the liquid phase to the solid phase. If sorption is fast compared to the groundwater flow velocity, the element will reach an equilibrium condition between liquid and solid phase. In other words, sorption is almost instantaneous and thus time-independent. This is called equilibrium sorption.

Inherent in the K_d – type 'linear isotherm' is the assumption that the K_d of the element of interest is independent of its concentration in the aqueous phase. In other words, K_d is a constant accounting for solute uptake processes that are kinetically fast and reversible. Linear sorption generally takes place at a low solute concentration where the sorption capacity of the sorbing solid is large relative to the available chemicals for sorption. Linear isotherms have been widely used as an approximation of the dilute end of the adsorption isotherm (US EPA 1999b). It has been used widely to describe solute retention by soils and aquifer sediments (Helfferich 1962; Sposito 1984; among others).

At low concentrations, sorption of most elements can indeed be described by means of the linear equilibrium sorption approach (Figure 4-1). At higher concentrations, the sorption sites become saturated and non-linear sorption isotherms such as the Freundlich equation with $b \neq 1$ may need to be considered. Further increasing the liquid phase concentrations does no longer increase the concentration on the solid phase. At a given point, the solubility limit of the element in the liquid phase is reached, and a precipitate (inorganics) or insoluble phase (organics) is formed. The maximum concentration in the liquid phase beyond which precipitation occurs is called the solubility limit, C_s . The solubility of organic and inorganic compounds may be affected (e.g. decrease) as a result of presence of certain chemicals in hydraulic fracturing fluids.



Figure 4-1 General sorption isotherm representation, showing differences between linear (indicated as " K_d " region) and non-linear sorption (indicated as "Freundlich" region), a transition period left of the precipitation threshold, and solute precipitation (indicated as "precipitation" region). Vertical axis (C_s) and horizontal axis (C_t) are, respectively, the sorbed concentration (on solid phases) and the dissolved concentration (in the liquid phase). Source: Wang et al. (2009).

The K_d is used together with the rock bulk density, ρ_b (g/cm³), and porosity, η (cm³/cm³), to calculate the retardation coefficient R_f (dimensionless)

$$R_f = 1 + \frac{\rho_b K_d}{\eta} \tag{2}$$

The retardation factor R_f defines the transport velocity of a retarded chemical relative to the transport velocity of a water molecule; for instance, a chemical substance with an R_f value of 10 will have a ten times slower transport velocity than a water molecule.

For organic compounds sorption and retardation will be determined from the fraction of organic carbon, f_{OC} (g/g), within geological formations available to adsorb organic compounds and the organic carbon partition coefficient K_{OC} (L/kg):

$$K_d = f_{OC} K_{OC} \tag{3}$$

Where experimental values of K_{OC} are not available, estimation methods based on the octanol-water partition coefficient K_{OW} (L/kg) have been used (e.g., using the US EPA EPI-Suite – US EPA 2012b).

Alternative strategies have been developed for inorganic chemicals (section 4.4). Possible interactions with geogenic components have been explored, as the hydrochemical background conditions may affect mobility and persistence.

Given the extreme conditions of temperature, pressure and redox, auxiliary determinations have been explored to establish any potential temperature, pressure and redox effects on chemical persistence and mobility (Sections 4.1.1.2 and 4.1.4).

4.1.1. Defining the hydrochemical conditions of deep groundwater: Gunnedah Basin

4.1.1.1. General hydrochemical parameters

Hydrochemical conditions were estimated for the main groundwater formations that are likely contributing to transport of hydraulic fracturing substances or geogenics. A summary of parameters based on a compilation of literature data is provided in Table 4-1. Most of the data are from CDM Smith (2014), unless otherwise indicated. Further details about the assumptions behind the parameter values are discussed here.

Namoi alluvium:

- The fraction of organic carbon (f_{OC}) available for sorption was estimated as follows. Assume soil organic carbon equal to 1-2% (Ward 1999, Table 14). Assume 1% OC in the soil surface layer, while at a depth of 1 m only 10% of surface amount remains (i.e. %OC = 0.1). The 0.1% (or f_{OC} = 0.001 g/g) is then considered constant with depth.
- Sand = quartz, therefore same assumptions as sandstone (i.e. minimal sorption); Gravel may have basalt some iron/ Al oxides and smectite; Alluvial plains soils (mean 44% clay); Clays in some soil is about 25% from basalt and 8-10% from sandstone parent materials.
- Redox potential measurements in Narrabri and Gunnedah Formation groundwater bores were positive (median values of respectively 92 and 109 mV) (NSW Office of Water 2011).

Pilliga sandstone:

Small amount of carbon is likely to be in carbonate form (Zheng et al. 2015), therefore assume little contribution of OC. Dominant constituents are quartz (~50%), Feldspar (~35%), Mica (~10%), chlorite and montmorillonite (1%). The most substantial proportion of reactive clay is mica. Higher sorption occurs on low charge density clays with low hydration cations (Boyd et al. 2011), where Ca and Na hydration radii could limit sorption. Nitroaromatics are strongly adsorbed by smectites (e.g. Handerlein and Schwerzenbach 1993), but its content is low. Boyd et al. (2011) suggests complex formation with cations. The above two processes could compensate for each other. HMX has similar properties to RDX; Jarramillo et al. (2011) suggest no sorption of HMX on mica and quartz.

Blythesdale Group:

- Blythesdale Group—composed of the Orallo Formation, Mooga Sandstone and Bungil Formation—contain predominantly fine grained sediments that are considered to be negligibly transmissive units (CDM Smith 2014).
- Lithology is clayey to quartzose sandstone, subordinate siltstone and conglomerate. For the purpose of assigning hydrochemical parameters, Blythesdale Group is considered similar to Pilliga Sandstone.
- Shales and siltstone will have some organic carbon; average for all shale 0.8 % TOC; assume 10% shale in the formation (i.e. %OC = 0.08).

Hoskisson seam:

- C content in bituminous coal = 65-80%, anthracite = 85-95% and lignite 55-70% (Simane et al. 2016). Assume C content is 75% as an average or 55% as a conservative value (not all C will participate in sorption due to diffusion limited kinetics, a process where sorption or uptake is time-dependent and generally slow, hence sorption will depend on residence time and flow conditions). Due to coals generally having surface areas¹⁴ around 200 m²/g (Thomas and Damberger 1976, Mahajan 1984, Linge 1989), the K_{oc} of carbonaceous materials is likely to be higher by 1-2 order of magnitude than non-coal carbon materials which to an extent could compensate for the kinetics effect that limit sorption.
- The seam is not 100% coal but lenses of coal in geological formation assume 50% coal (i.e. 50% OC). Higher TDS means lower solubility and higher sorption but this is expected to be a small effect especially where solubility is either low. Sorption on carbonaceous materials is often non-linear but since the concentrations of chemicals are likely to be low (high volume of water) or high (net effect small) we therefore assume linearity. Based on six exploration wells, the average thickness of Hoskissons and Maules Creek coal seam is 7.3 and 4.3 m, respectively (Eastern Star Gas 2008).

Maules Creek Formation (upper):

- No hydrochemistry data were found for this formation. Because its lithology is similar to the underlying Maules Creek Formation (coal measures), its hydrochemistry is also considered similar. Its organic carbon content is treated as per Pilliga Sandstone.
- To allow for temperature corrections of sorption parameters, the temperature range was estimated based on a selection of wells located within the study area (Figure 4-2), assuming i) an average thickness of 50 m overlying the Bohena coal measures (Eastern Star Gas 2008), and ii) an average temperature gradient of 18.3 °C/km from surface to 800 m (see Figure 4-3) and 42.5°C/km from 800 to 1200 m (see Figure 4-3).

Maules Creek Formation (Bohena coal measures):

- Generally contains eleven distinct coal seam, 1.5 to 3.5 m thick; assume coal seam represents half the formation thickness. Assume similar conditions to Hoskisson seam.
- To allow for temperature corrections of sorption parameters, the temperature range was estimated assuming i) that the Bohena coal measures occupy depths ranging from 500 to 1000 m (CDM Smith 2014), and ii) an average temperature gradient of 18.3°C/km from surface to 800 m (see Figure 4-3) and 42.5°C/km from 800 to 1200 m (see Figure 4-3).

Maules Creek Formation (lower):

- Treat as per Pilliga sandstone.
- To allow for temperature corrections of sorption parameters, the temperature range was estimated assuming i) an average thickness of 50 m underlying the Bohena coal measures (Eastern Star Gas 2008), and ii) an average temperature gradient of 18.3°C/km from surface to 800 m (see Figure 4-3) and 42.5°C/km from 800 to 1200 m (see Figure 4-3).

 $^{^{14}}$ The internal surface area of the coal (measured by CO₂ adsorption), which is generally several orders of magnitude greater than the external surface area

Geology	Lithology	Relative proportion Mineral /clay type	рН	TDS (mg/L)	Temperature (°C)	Hydrostatic pressure ¹⁵ (m)	Carbon content (%)	Redox status	Microbial activity status (low, medium, high)
Namoi alluvium	gravel/sand	mostly quartz	7–9 (8*)	300–3,000 (700 [*])	Assume surface conditions	64 – 123 (88 [*])	0.1	Oxidising	Medium (aerobic for shallow groundwater, anaerobic for deeper groundwater)
Pilliga sandstone	Sandstone	mostly quartz with conglomerates (silica), minor silt	7–8 (7.6*)	500-6,000 (900*)	20-58 (40*)	67 – 427 (125 [*])	0	Oxidising/ Reducing	Low (anaerobic)
Blythesdale Group	medium- to coarse-grained sandstone, siltstone and shale	mostly quartz with conglomerates (silica), minor silt and mudstone	n.d.	n.d.	28-28.5 (28.3 [#])	1 — 197 (39 [*])	0.083	Reducing	Low (anaerobic)
Hoskisson seam	coal and mudstone	interbedded coals, silts and quartzose channel sands	7-9 (7.7*)	600-18520 (11,800 [*])	46.9-47.8 (47.4 [#])	362 – 815 (708*)	55	Reducing	Low (anaerobic)
Maules Creek Formation (upper)	siltstone, sandstone and mudstone	mostly quartz, feldspar, and lithic conglomerates	n.d.	n.d.	36 – 49 [@]	282 – 1010 (827*)	0	Reducing	Low (anaerobic)
Maules Creek Formation (Bohena coal measures)	Coal and mudstone	mostly quartz, feldspar, and lithic conglomerates	6-9.4 (7.6 [*])	300-1,780 (677*)	37 - 51 [@]	602 – 1019 (908*)	55	Reducing	Low (anaerobic)
Maules Creek Formation (lower)	siltstone, sandstone and mudstone	mostly quartz, feldspar, and lithic conglomerates	n.d.	n.d.	38– 53 [@]	283 – 1058 (828*)	0	Reducing	Low (anaerobic)

Table 4-1 Summary of hydrochemical conditions for Gunnedah basin geology (Well completion report). Hydrostatic pressure based on 15 locations within the study area. * = median; # = mean; @ = estimated; n.d. = no data.

¹⁵ Hydrostatic pressure increases in proportion to depth measured from the surface because of the increasing weight of fluid

4.1.1.2. Defining temperature and pressure conditions of deep groundwater

Temperature and pressure conditions of groundwater formations that are likely contributing to transport of hydraulic fracturing substances or geogenics are important variables as they determine properties such as chemical solubility of dissolved gases, general reactivity (adsorption/desorption), and microbiological transformation processes. Abiotic processes are expected to increase proportionally with temperature so that an increasing temperature will lead to an increase in hydrolysis rates.

For instance, gas solubility decreases with increasing temperature and salinity and increases with increasing pressure. The effects are non-linear in all cases. For methane, a temperature difference of 20°C (e.g. between 10 and 30°C) for fresh water (zero salinity) results in a difference in solubility of 10 mg/L/atm. At 20°C, methane solubility ranges from 25 mg/L for fresh water to 19.3 mg/L at 40,000 mg/L salinity (Mallants et al. 2016).

Temperature profiles were obtained from well completion reports listed on the NSW online Digital Imaging of Geological System (DIGS) database. Figure 4-2 shows nearly one hundred boreholes with temperature profiles within the CDM Smith groundwater model area. A subset of five boreholes was selected for detailed analysis; all wells are located within the study area (Figure 4-2). The recorded temperature profiles from these five wells are combined in Figure 4-3. Average temperature gradients were calculated from surface to 800 m depth and from 800 to 1200 m depth; at 800 m depth a break in the temperature slope is evident, which was the reason for calculating two temperature gradients. From surface to 800 m the gradient is 18.3°C/km, while from 800 to 1200 m it is 42.5°C/km. The methodology to estimate temperature effects on sorption parameters is discussed in Sections 4.1.4.1 and 4.1.4.3.3.

The pore pressure – depth relationship was derived from simulated hydraulic head values using the CDM Smith groundwater model.



Figure 4-2 Left: Boreholes with available temperature profiles in the CDM Smith groundwater model area. Right: five boreholes with temperature profile selected for the current study (orange polygon).



Figure 4-3 Measured temperature profiles for five boreholes within the study area.

4.1.2. Defining the hydrochemical conditions of deep groundwater: Surat Basin

4.1.2.1. General hydrochemical parameters

Hydrochemical conditions were estimated for the main groundwater formations in the Surat Basin that potentially could provide a pathway for transport of hydraulic fracturing substances or geogenics. In the selected test case area, the following major aquifers were identified as being of relevance for the current assessment: Dawson River alluvium, BMO Formations, Gubberamunda Sandstone, Westbourne Formation, Springbok Formation, Walloon Coal Measures, and Hutton Sandstone. Underlying the Hutton Sandstone is the Evergreen Formation, a low-permeability formation that is considered an aquitard (i.e. does not contribute to groundwater flow). Because of its separating properties, the Evergreen Formation is an effective barrier against chemical substances ending up in the underlying Precipice aquifer; for this reason the Precipice is not considered in the current analysis. A summary of parameters for these formations based on a compilation of literature data is provided in Table 4-1. All data on the mineralogy of groundwater formations are derived from Grigorescu (2011) unless stated otherwise. Further details about the assumptions behind the parameter values are discussed here.

Dawson River alluvium:

The fraction of organic carbon (OC) available for sorption was estimated as following the example of the Namoi River alluvium in the Gunnedah Basin. Assume soil organic carbon equal to 1-2% (Ward 1999, Table 14). Assume 1% OC in the soil surface layer, while at a depth of 1 m only 10% of surface amount remains (i.e. %OC = 0.1). The 0.1% (or foc = 0.001 g/g) is then considered constant with depth.

- Sand is mainly quartz, therefore use same assumptions as for sandstone (i.e. minimal sorption); gravel may have basalt, some iron/aluminium oxides and smectite; alluvial plains soils (contain on average 44% clay); clays in some soil is about 25% from basalt and 8-10% from sandstone parent materials.
- No redox potential data (E_h) are available on the Dawson River alluvial groundwaters in the Queensland Department of Natural Resources and Mines (DNRM) groundwater database (2015). Redox-sensitive parameters such as iron and manganese appear to be very low (i.e. below the detection limit). Together with the shallow depth of the Dawson River alluvium, it is assumed that redox conditions in the Dawson River alluvium are generally positive (i.e. oxidising).
- Groundwater quality in the Dawson River alluvium ranges from fresh to saline (101-10,281 mg/L, with a median of 411 mg/L; QLD DNRM groundwater database, 2015).

Gubberamunda Sandstone:

- The Gubberamunda Sandstone, together with the Westbourne Formation and Springbok Sandstone, is considered as the lateral equivalent to the Pilliga Sandstone (Totterdell et al. 2009). A small amount of carbon is likely to be in carbonate form (Zheng et al. 2015), therefore assume little contribution of OC. Dominant constituents are quartz (~30-90%) and kaolinite is the dominant clay mineral (up to 30%). Feldspar varies between ~8-28%, and plagioclase is always dominant over K-feldspar. The concentration of mica is highly variable, and can reach up to 20% in some wells; siderite and hematite-rich units are rare, and calcite was not detected.
- Groundwater quality in the Gubberamunda Formation ranges from fresh to brackish, with TDS concentrations in the range from 215-5,900 mg/L (median 770) (Mallants et al. 2016).

Westbourne Formation:

- The dominant constituents of the Westbourne Formation are quartz (~18-80%) and feldspar (~12-40%; plagioclase is always dominant). Kaolinite (up to 30%) is the dominant clay mineral. The concentration of mica is generally less than 5%, but can be higher (up to 14%) in some samples. Chlorite is present in some samples and siderite and hematite-rich bands are frequent, whereas calcite occurrence is rare.
- Groundwater quality in the Westbourne Formation ranges from fresh to saline, with TDS concentrations in the range from 228-17,700 mg/L (median 1070) (Mallants et al. 2016).

Springbok Sandstone:

- The dominant constituents of the Springbok Sandstone are quartz (~17-71%) and feldspars (5-46%). Kaolinite is the dominant clay mineral (5-25%). Plagioclase is always higher than other feldspars and can comprise up to 36%. The concentration of mica is generally below 5%, but reaches 17% in one sample. Chlorite occurs only as traces with up to 2% in a few samples. Siderite and hematite-rich bands are frequent, whereas calcite veins are rare.
- Groundwater quality in the Springbok Sandstone ranges from fresh to saline, with TDS concentrations in the range from 600-12,200 mg/L (median 1540) (Mallants et al. 2016).

Walloon Coal Measures:

• Quartz is generally the main component (6-65%) and kaolinite the dominant clay mineral (2-68%). Feldspars vary significantly (2-57%). Plagioclase is generally dominant (up to 47%). In some samples, plagioclase also dominates over quartz. The concentration of mica is generally low but reaches up to 14% in some samples. Chlorite is generally minor (up to 5%). Siderite is ubiquitous and calcite veins are common. Magnesium carbonates (dolomite and ankerite) are also present within the Walloon Coal Measures. Within the Walloon Coal Measures, there appear to be distinct differences of the mineralogy related to the depositional environment (channel, floodplain and peat/swamp). Channel sediments contain more quartz and have lower concentrations of clay minerals than the floodplain sediments. Mires are generally clay-rich (25-75%).

- Fixed carbon content of the Walloon Coal Measures ranges from 4.3-46.7 weight %, with a mean of 31.5% (Scott et al. 2007). Scott et al. (2007) described the coals of the Walloon Coal Measures in the Surat Basin as dull, and rich in carbon (>80% dry, ash-free). They have a high volatile matter content (>30% as received), and the coal rank ranges from sub-bituminous to high-volatile bituminous.
- The lithological composition of the Walloon Coal Measures is highly variable (e.g. Grigorescu (2011) and Esterle et al. 2013) due to a variable depositional environment (channel, floodplain and mires). Papendick et al. (2011) suggested that average wells near Roma have a net coal thickness of 15 m, which increases to 20-30 m near Dalby over a thickness of approximately 250-500 m.
- Groundwater quality in the Walloon Coal Measures in the northern Surat Basin is spatially highly variable depending on the regional processes (e.g. groundwater recharge). It is generally in the range from fresh to saline, with TDS concentrations in the range from 109-16,800 mg/L (median 1700) (Mallants et al. 2016; APLNG 2015).

Hutton Sandstone:

- Quartz is generally the main component (25-94%) and kaolinite is the dominant clay mineral (2-37%). Feldspar varies throughout the formation (2-23%), and with few exceptions, plagioclase is the dominant feldspars but vary significantly (2-57%). The concentration of mica is highly variable and can be up to 27%; siderite and calcite veins are also present.
- Similar to the Walloon Coal Measures, the lithological composition of the Hutton Sandstone is highly variable in accordance with its deposition, i.e. fluvial and tidally-influenced deltaic channels, crevasse splay and floodplain environments (Guiton et al. 2015).
- Groundwater quality in the Hutton Sandstone in the northern Surat Basin is fresh to saline, with TDS concentrations ranging from 96-10,200 mg/L (median 590) (APLNG 2015).

Table 4-2 Summary of hydrochemical conditions for Surat basin geology. 1 = Grigorescu (2011); 2 = Gopalakrishan et al. (2015); 3 = Esterle et al. (2013). 4 = Mallants et al. (2016). 5 = Scott et al. (2007). 6 = APLNG (2015); 7 = Papendick et al. (2011). 8 = Queensland Department of Natural Resources and Mines (2015).

Geology	Lithology	Relative proportion: Mineral /clay type	рН	TDS (mg/L)	Temp.	Hydrostatic pressure ¹⁶ (m)	Carbon content (%)	Redox status
Dawson River alluvium	Gravel, silt, clay and sand	Mostly quartz	6-8.9 (median 7.9) ⁴	101-10,281 (median 411) ⁸	Surface conditions		0.1	Oxidising
Bungil Formation- Mooga Sandstone- Orallo Formation (BMO Group)	Orallo Formation: Sandstones are largely friable, medium to coarse-grained, partly calcareous; minor siltstone, mudstone and coal beds are present. The occurrence of bentonitic tuffs indicates. contemporaneous volcanic activity ¹ . Bungil Formation: this geological unit consists mainly of fine-grained lithic sandstones, interbedded with siltstones and mudstones. Minor sublabile to quartzose sandstones occur ¹ .	Orallo Formation: Quartz is the main component (30-68%) and kaolinite is the dominant clay mineral (up to 22%). Bungil Formation: Quartz ranges between 38-46%; the concentrations of fieldspars are very high (often more than 50%). Plagioclase is always dominant. Kaolinite can reach up to 20%. Mica is approximately 5%. No information was available for the Mooga Sandstone ¹ .	1) 4.8-8.8 (median 7.5) ⁴ 2) ~5.8-11.7 (median 8.5) ⁶	1) 215-5900 (median 770) ⁴	16-36.5 (median 25.60) ⁴	280-302	0	Reducing
Gubberamunda Sandstone	Medium- to coarse-grained, largely quartzose, poorly sorted sandstone with minor conglomerates and siltstones ¹ .	Quartz is main component (30- 90%); feldspars vary (8-28%) with plagioclase always dominant. Kaolinite (up to 30%) is the	1) 5.7-8.8 (median 8.2) ⁴	1) 215-5,900 (median 770) ⁴	16-36.5 (median 25.60) ⁴	280-302	0	Reducing

¹⁶ Hydrostatic pressure increases in proportion to depth measured from the surface because of the increasing weight of fluid

		dominant clay mineral. Small concentrations (only a few percent) of mixed-layer clays are smectite-rich ¹ .	2) ~5.8-11.7 (median 8.5) ⁶					
Westbourne Formation	Very fine- to medium-grained, fairly to poorly sorted, sublabile to quartzose, often massive sandstones with laminated to thinly-bedded siltstones and shales ¹ .	Quartz is main component (18- 80%) with feldspars (12-40%); plagioclase is always dominant. Kaolinite (up to 33%) is the dominant clay mineral. The mixed-layer clays are highly variable ¹ .	1) 6.8-8.6 (median 7.6) ⁴ 2) ~8-9.3 (median 8.8) ⁶	1) 228-17,700 (median 1,070) ⁴	17.3-27.3 (median 23.45) ⁴	220-300	0	Reducing
Springbok Sandstone	Feldspathic sublabile to lithic sandstone, sometimes porous, friable, pebbly or with calcareous cement; andesitic debris and bentonitic tuffs from contemporaneous volcanism ¹ .	Consists of quartz (17-71%) and plagioclase always the dominant feldspar. Kaolinite (5-25%) is the dominant clay mineral. Mixed- layer clays are smectite- dominant ¹ .	1) 6.7-8.1 (median 7.3) ⁴ 2) ~7.4-11.8 (median 8.5) ⁶	1) 600-12,200 (median 1,540) ⁴ 2) 225-10,400 (median 1,820) ⁶	22.7-28.9 (limited data) ⁴	217 - 284	0	Reducing
Walloon Coal Measures	Labile sandstone, siltstone, mudstone and coal, with lesser calcareous sandstone, impure limestone, tuff and ironstone nodules (siderite) ^{2, 3} .	Quartz is generally the main component (6-65%) and kaolinite is the dominant clay mineral (2- 68%). Feldspars vary significantly (2-57%). K-feldspars are usually around 5%. Plagioclase is consistently dominant (up to 47%) and sometimes dominates over quartz. Siderite is ubiquitous and calcite venes are common. Magnesium -carbonates (dolomite and ankerite) are also present ¹ .	1) 6.7-9.1 (median 8.0) ⁴ 2) ~7-9.8 (median 8.0) ⁶	1) 109-9,980 (median 1,700) ⁴ 2) 90-16,800 (median 3,830) ⁶	21.8-39.1 (median 25.25) ⁴	216 - 300	4.3-46.7 (mean 31.5) ⁵	Reducing

Hutton	White to light grey, fine- to	Quartz is the main component	1) 6.5-9.3	1) 119-3,260	19.6-46.9	220 - 280	0	Reducing
Sandstone	medium-grained, sublabile to	(25-94%) and kaolinite (2-37%) is	(median 8.3) ⁴	(median 665) ⁴	(median			
	quartzose sandstone, with dark	the dominant clay mineral.			26.80) ⁴			
	grey micaceous or	Mixed-layer clays are smectite-						
	carbonaceous siltstone	rich ¹ .	2) ~6.4-10.9	2) 96-10,200				
	interbeds ¹ .		(median 8.0) ⁶	(median 590) ⁶				
Sandstone	medium-grained, sublabile to quartzose sandstone, with dark grey micaceous or carbonaceous siltstone interbeds ¹ .	(25-94%) and kaolinite (2-37%) is the dominant clay mineral. Mixed-layer clays are smectite- rich ¹ .	(median 8.3)* 2) ~6.4-10.9 (median 8.0) ⁶	(median 665)* 2) 96-10,200 (median 590) ⁶	(median 26.80) ⁴			

4.1.2.2. Defining temperature and pressure conditions of deep groundwater

Temperature profiles were obtained from well completion reports provided by QLD DNRM. Figure 4-4 shows the recorded temperature profiles from three wells within the case study area. An average temperature gradient of 23°C/km was calculated from surface to 1000 m depth.

The pore pressure – depth relationship was derived from simulated hydraulic head values using the OGIA groundwater model.



Figure 4-4 Measured temperature profiles for three boreholes within the Surat case study area (data source: Queensland DNRM).

4.1.3. Methodology for adapting the attenuation parameters obtained from literature to

site-specific values

For some organic compounds the literature values of key attenuation parameters (namely K_{OC} and half-life $t_{1/2}$) are unlikely to have been obtained under the conditions truly reflective of the geology of the sites being investigated in this project. For example, the K_{OC} and half-life measured under controlled laboratory conditions in a surface soil, or even aquifer material, is unlikely to be representative of that in the geological formations and coal seams. Most published studies on organic compounds tend to be from soils or materials from shallow aquifers, whereas the effective K_{OC} of an organic compound on highly carbonaceous materials under saline conditions is likely to be much higher than that estimated based on such studies. For some compounds such as nitro-aromatics (similar to HMX), clay minerals have been found to be highly sorptive (Weissmahr et al. 1997). However, the K_{OC} values from the literature may not reflect the contribution that clay and other mineral matters can make to the potential sorption of some organic compounds in a certain geological formation with limited organic carbon content. It is also noteworthy that on highly carbonaceous materials such as coals, the sorption of organic chemicals has often been found to be concentration dependent (Dell Site 201). However, since the concentrations of chemicals during the hydraulic fracturing operations are expected to be generally low, it is assumed that sorption is independent of concentration and hence the concept of K_{OC} or better, K_d (linear reversible sorption) is acceptable. This is in line with the assumption of linear and reversible sorption discussed in Section 4.1.

Similarly, the rate of breakdown of organic substances (half-life) at depths in coal seams where hydraulic fracturing chemicals are introduced, may be significantly different than that in surface soil due to their higher temperature, different microbial environment and redox status.

Because of the specific geological and environmental conditions that determine sorption (organic and inorganic substances) and degradation (organics only), the literature values need to be adapted for the specific conditions associated with the study site. The approach adopted here therefore defines first a generic set of default sorption and half-life parameters (Section 4.3.3), which are subsequently adapted to represent more site-specific conditions (Section 4.3.3.1).

4.1.4. Effect of key physicochemical variables on contaminant attenuation parameters

In this section, the effects of key variables pressure, temperature and pH on attenuation processes affecting organic compounds and inorganic substances in deep groundwater systems are considered. By their nature, inorganic non-radioactive substances are persistent and do not undergo degradation. Consequently, only the effects of pressure, temperature and pH on inorganic sorption reactions are considered.

The effects of these variables are considered with respect to two specific scenarios related to deep groundwater in this study.

- The effect of physico-chemical variables on the attenuation of geogenic contaminants that might be present in the coal seams. This represents an unperturbed system where the variables may impact on the dissolved concentrations of some geogenic contaminants. The temperature in deep groundwater systems is expected to be as high as 60°C.
- The injection of hydraulic fracturing fluids that experience a much higher pressure at great depth than atmospheric pressure. It is expected that the in-situ pore pressure may reach up to about 13 MPa. The effect of pressures associated with the hydraulic fracturing itself is likely to be localised and transitory in nature and considered to have a negligible effect.

4.1.4.1. Effect of temperature on degradation of organic compounds

The temperature dependence of reactions such as biodegradation and hydrolysis is well established and can be incorporated using the Arrhenius equation. This relationship states that the reaction rate constant κ in homogeneous solutions and consequently the reaction half-life $t_{1/2}$ (assuming first-order kinetics $t_{1/2} = (\ln 2)/k$) depends on the activation energy E_a of the reaction and the temperature at which the reaction occurs. The Arrhenius relationship can be presented as (Stumm and Morgan 1981):

$$\kappa = A \, exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where κ is the rate constant (1/day), A is *the* rate coefficient at infinite temperature (1/day), E_a is activation energy (kJ/mol), R is the gas constant (0.008314 kJ/K/mol) and T is absolute temperature (K).

Based on first-order kinetics, Equation (4) can be reformulated to (EFSA 2008):

$$t_{1/2,T1} = t_{1/2,T2} \left(\frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \right)$$
(5)

where $t_{1/2,T_1}$ and $t_{51/2,T_2}$ are the half-lives at temperatures T_1 and T_2 , respectively. $t_{1/2,T_1}$ may also be written as:

$$t_{1/2,T1} = t_{1/2,T2} exp\left(lnQ_{10}\left[\frac{T_2 - T_1}{\Delta T}\right]\right)$$
(6)

where Q_{10} is defined as the ratio of pesticide degradation rate coefficients (k_2/k_1) at a temperature T_1 that is 10°C lower than a temperature T_2 , i.e. where ΔT is equal to 10°C.

Based on Equations (5) and (6) the following relationship can be derived between Q_{10} and E_a :

$$Q_{10} = exp\left(\frac{\Delta T E_a}{R T_1 T_2}\right) \tag{7}$$

The Arrhenius relationship is based on ideal conditions. As the activation energy E_a of a particular compound varies, the Q_{10} will vary accordingly and also in different matrices (soil, water, sediment, etc.). Therefore, there is no universal value of Q_{10} for all compounds. However, the Q_{10} approach has commonly been used for predicting organic compounds behaviour in real environments. The theory has been widely applied for certain organic compounds such as pesticides, where a considerable body of literature exists on the effect of temperature on the rate of reaction to test the theory.

In 2008, a European expert panel considered the compound specific E_a values of pesticides and based on actual measured data (99 dataset) for 53 pesticides suggested a Q_{10} value of 2.58 (EFSA 2008). This was essentially an update on a previous value of 2.2 that was used in modelling of pesticide fate in soil and groundwater since 1997.

For hydrocarbons a Q_{10} of 2.0 has been commonly used for degradation in groundwaters (van Stempvoort and Biggar 2008). A more recent study (Bagi et al. 2013) based on 32 data sets on biodegradation of hydrocarbons in marine water suggested a large variation in Q_{10} values (1.1 to 16.2 with a mean of 2.8, with about half the cases falling below and the other half above 2.0). The same research group (Bagi et al. 2014), working on naphthalene degradation in Arctic and temperate seawaters at different temperatures (0-15°C), found that the naphthalene degradation showed similar Q_{10} ratios (3.3-3.5) in two different quality seawaters. The similarity in these values despite different microbial community compositions between two types of waters is possibly due to the narrow temperature range studied. They also noted that the temperature dependence of naphthalene was different to that of sodium-benzoate supporting the earlier observation about the compound-specific nature of E_a .

The above discussion shows that a single value of Q_{10} for a range of organic compounds and extrapolation between different systems (soil versus water) is fraught with difficulties. Most of the studies in literature on Q_{10} have been generated to extrapolate data to colder climate (e.g. Arctic climate) rather than warmer conditions. The temperature gradient from the soil surface to deep ground waters is shown to range from 20 - 60°C (Sections 4.1.1.2 and 4.1.2.2), whereas some of the guidance in literature allow the use of Q_{10} to a maximum of 30°C, especially for biodegradation processes.

Given the complexity of the processes involved and the paucity of data on the effects of temperature on the degradation of a vast majority of compounds studied here, it was decided that the following approach be used for deep groundwater studies:

- Use the Q₁₀ values from water based systems (e.g. marine waters) rather than from surface soils.
- Use the Q₁₀ default value of 2.0 commonly used in current models such as the oil spill contingency and response (OSCAR) model for marine water systems (Reed et al. 1994).
- Only allow temperature adjustment of half-life to 30° C, beyond which it is assumed that rate of degradation does not increase proportionately to Q_{10} but is also not limited by temperature. This assumes no thermophilic community that is previously adapted to the chemical of interest and no detrimental impact of temperature on the microbial activity.

The above approach is likely to result in a conservative estimate of any increases in half-life at higher temperatures prevailing in deep ground waters. The higher the temperature increase, relative to the reference temperature, the greater the degree of conservatism.

If the conservative estimate coupled with long travel times from the contaminant source to receptors allows sufficient attenuation of the compound than no further investigation is warranted.

4.1.4.2. Effect of pH, temperature and pressure on sorption coefficients of organic compounds

4.1.4.2.1. pH

Many organic compounds have varying degree of polarity and some are ionisable (e.g. phenols, amines) and therefore their sorption or partitioning behaviour between solid and solution phases are pH sensitive. The ionisation state of the chemical has a marked impact on its solubility, sorption, transport and bioavailability. For example, an acidic compound on dissociation at a certain pH will produce an anion (negatively charged) which may have limited affinity to net negatively charged clay minerals or aquifer materials, whereas a basic compound in a cationic state (positively charged) is likely to be sorbed through cation exchange mechanism on such materials. In the neutral (undissociated) form, an organic compound is likely to sorb or partition to organic matter through hydrophobic interactions and van der Waals forces. Therefore, a neutral form of an acidic compound and the protonated form (and thus positively charged) of a basic molecule are both most favourable to sorption onto aquifer materials.

The ionisability of an organic compound is represented by its dissociation constant (pKa), which determines its likely charge state (neutral or ionic) in the ambient environment being considered, i.e. deep groundwater in this study. At the pH equal to the specific pKa of a compound, 50% of the molecules are expected to be in the ionised form. As a thumb rule, a compound is responsive to the pH of the system approximately 2 pH units above and below its pKa value. For example, methyl-phenol being considered in the present study has a *pKa* of 10.3, which means that in the deep groundwaters of the Gunnedah basin (with pH in the range of 7.6 to 8.0), only a very small fraction is expected to be in the anionic form that has little sorption affinity to aquifer material other than organic carbon.

In this study the effect of pH on the sorption of the ionisable compound has been taken into consideration by choosing the values from the literature at the relevant pH or adjusting the K_d based on their established pH relationship from literature, where available.

The effect of pH perturbations associated with acidification pre-treatments of boreholes and pH modifiers in hydraulic fracturing fluids on the sorption of organic compounds (e.g. K_{OC} values) was not considered. These effects are likely to be short-lived as the introduced acidity will be neutralised by components of the coal, near-wellbore rock, and groundwater system (e.g. dissolution of carbonate minerals and initiate fissures in the rock) and also attenuated by dilution.

4.1.4.2.2. Temperature

Sorption of organic compounds to the solid phase (organic matter, clays, iron oxides etc.) is known to be temperature dependent and can be described by the Van't Hoff equation:

$$lnK_{eq} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{TR}$$
(8)

where K_{eq} is the equilibrium partition coefficient at a given temperature (L/kg), Δ H is the change in enthalpy (KJ/mol), Δ S is the change in entropy (KJ/mol/K), T is absolute temperature (degrees Kelvin), R is the universal gas constant (8.314 x 10⁻³ kJ/K/mol).

The slope (Δ H/R) in the above equation is negative for an endothermic sorption and positive for an exothermic sorption and thus depends on the compound in question.

Sorption of particular PAHs (naphthalene, phenanthrene and pyrene) on low organic carbon aquifer sediments has been found to be an exothermic process and as a result sorption was found to decrease with increasing temperatures, with changes in the order of 1.1 to 1.6 with an increase in temperature from 4 to 26°C (Piatt et al. 1996). Similarly, sorption of phenols on clays has been found to be exothermic (Snoyeink et al. 1969), but the temperature effect was noted to be relatively small in this case.

Most studies in the literature have been carried out at temperatures that do not cover the temperature range in deep groundwaters at our study sites (20-60°C). However, in a study on transport of hydrocarbons (naphthalene, toluene, perchloroethylene) through soil columns packed with silty gravel till aquifer material at 20, 50 and 90°C, Steep and McLure (2001) observed that retardation factors (by implication sorption) of naphthalene and perchloroethylene decreased by half when the temperature was raised from 22-25 to 90 °C. They noted the temperature effect increased with increasing molecular weight and decreasing solubility of the compound. This indicates that the temperature effect is likely to have a greater impact on more hydrophobic compounds (e.g. PAHs) than the polar compounds (e.g. phenols) considered in the present study.

Based on the above arguments it was decided here that the temperature adjustment is only likely to be of any significant consequence on the compounds that have $\log K_{ow} > 3.0$ (e.g. naphthalene). Considering the relevance of Steep and McLure (2001) to the current study, a 10% reduction in sorption was assumed with every 10°C increase in temperature (above 20°C) in the geological model layers being considered, as a conservative estimate.

4.1.4.2.3. Pressure

Generally pressure has little effect on solubility of most liquids. However, for volatile compounds the effect of pressure on the solubility and sorption of compounds is determined by the impact on its vapour pressure. For example, effect of pressure on the solubility of a volatile hydrocarbon (e.g. benzene) in a liquid will be determined by the impact on its partial pressure according to Henry's Law. Henry's Law, in simple terms, states that a given temperature the solubility of a gas in liquid is determined by its partial pressure.

Literature on the effect of pressure (at constant temperature) on the solubility of hydrocarbons, such as benzene and alkylbenzenes, in water have been found to increase with pressure and show a maxima in the range of 140-200 MPa (Sawamura et al. 1989). An increase was noted in the relative solubility of benzene and ethylbenzene from 1.0 to 1.035 and 1.037, respectively, with an increase in pressure from 0.1 to 25 MPa. The combined effect of temperature and pressure on solubilities of toluene showed that its relative solubility increased from 1.09 at 0.1 MPa and 298.2°K to 1.23 at 25 MPa and 313.2°K, indicating that temperature had a relatively greater effect than pressure on solubility (Sawamura et al. 2001).

Based on the above, the effect of pressure on solubility enhancement for such compounds is expected to be small in the pressure gradient expected in the deep groundwater studied here (maximum 13 MPa). Furthermore, the relationship between pressure and solubility of compounds is likely to be influenced by the presence of salts and other chemicals such as surfactants in water (e.g. Jaoui et al. 2002). The pressure impact during hydraulic fracking process is likely to be transitory in nature, considering the long travel times through the geological formations. Therefore the effect of pressure on the set of organic compounds considered in the current study were deemed to be of relatively minor importance compared to the uncertainty of the sorption parameters that are extrapolated from other systems.

4.1.4.3. Effect of pH, temperature and pressure on sorption coefficients for inorganic chemicals

4.1.4.3.1. pH

Changes in the pH of solutions may affect the extent of sorption processes by changing the aqueous speciation of chemicals in solution and by changing the surface charge of the mineral surfaces that possess ionisable functional groups (e.g. metal hydroxides). Surface ionisation is particularly important for adsorption reactions that are dominated by electrostatic interactions such as those involving alkali earth and alkali metals. The pH of zero charge (pZC) is an important parameter describing the ionisation properties of minerals in solution and the effects of pH (Stumm and Morgan 1996). In acidic solutions protons will also compete for binding sites.

Consistent with the approach for the organic chemicals, the effect of pH perturbations associated with acidification pretreatments of boreholes and pH modifiers in hydraulic fracturing fluids on the sorption of metals was not considered. These effects are likely to be short-lived as the introduced acidity will be neutralised by components of the coal, nearwellbore rock, and groundwater system (e.g. dissolution of carbonate minerals and initiate fissures in the rock) and also attenuated by dilution.

Examples of how pH affects the solution speciation of arsenic and uranium in solution are given in Figure 2-14 and Figure 2-15, respectively. Similar speciation versus pH plots for most common trace metals are available in the scientific literature.

Understanding the effect of pH changes on inorganic adsorption reactions is complex and needs to be done on a case by case basis taking into account the physicochemical properties of the inorganic contaminant and the sorbing phases. There are, however, some generalities that can be drawn from previous research. For instance, it is well established that for many metals there is a minimum pH known as the 'adsorption edge' below which the extent of adsorption declines dramatically (Tessier 1992). Typically, the adsorption edge lies in the pH range of 4 to 6 (Tessier 1992). In practice, the effects of pH will be minimal in the Gunnedah and Surat groundwater systems as monitoring data show that median pH for the various strata ranges from 7.6 to 8.0 for Gunnedah formations (Table 4-1) and from 7.3 to 8.8 for selected Surat formations (Table 4-2).

4.1.4.3.2. Effect of pressure on sorption reactions involving inorganic chemicals

From a purely thermodynamic perspective, the fundamental equation describing the effect of pressure on chemical equilibria (Marquis and Matsumura 1978) is as follows:

$$\left(\frac{\partial \ln K_p}{\partial P}\right)_T = -\Delta V /_{RT} \tag{9}$$

where K_p is the equilibrium constant (dimensionless), P is the pressure (Pa), ΔV is the volume change of the reaction (mL), R is the universal gas constant (8.314 x 10⁻³ kJ/K/mol) and T is the temperature (°K).

The negative sign in equation (9) means that if InK for a given chemical equilibrium increases with increases in pressure then ΔV is negative. Most chemical reactions result in a volume change because the sum of the partial molar volumes of products is generally not equal to that of the reactants. The volume change arises primarily from changes in the reacting species. In addition there may be changes in the solvent or suspending medium that results in volume changes. One of the most common examples is electrostriction of water in the vicinity of ions that results in contraction of the medium. The volume change ΔV , can be measured experimentally at controlled temperature and pressure. Volume changes for simple, monomeric reactions are relatively small, less than 30 mL/mol (Marquis and Matsumura 1978).

The effect of pressure on the extent of adsorption reactions is not clear. Some information on the stability of various mineral phases is available from the oceanographic research literature because of the need to understand the effects of pressure in the deep oceans. Most biological reaction rates are greatly reduced at pressures >300 atmospheres; many abiotic reactions, on the other hand, are accelerated. In terms of inorganic reactions, high pressure will significantly affect proton equilibria and mineral dissolution. For instance, the pH of seawater is 0.15 units lower at 4000 m depth than that at the ocean surface owing to pressure effects (Byrne and Laurie 1999). Despite an extensive search of the scientific literature, no practical studies could be found where the effect of pressure on the sorption of inorganic chemicals onto solid surfaces has been studied over an appropriate pressure range that is relevant to this study. It was therefore not possible to draw any general conclusions from the available studies that are directly applicable to the Gunnedah and Surat Basin groundwater systems.

4.1.4.3.3. Effect of temperature on sorption reactions involving inorganic chemicals

In the Gunnedah Basin the geothermal gradient is quite significant and water temperature ranges from 25 - 30°C in surface strata to a maximum of 58°C at depths of 1200 m. Similar temperatures have been recorded in the Surat Basin, i.e. from 30°C at the surface to 50-50 °C at 1000 m depth. Temperature is therefore likely to exert an important effect on chemical

reactions. From a theoretical perspective, the effect of temperature on adsorption reactions will depend on the thermodynamics of the reactions involved. For elements where adsorption is an exothermic process, K_d will decrease as temperature increases whereas for elements where adsorption is an endothermic process, K_d will increase as temperature increases (Stumm and Morgan 1996). Despite an extensive search of the scientific literature, very few practical studies could be found where the sorption of inorganics onto solid surfaces has been measured over an appropriate temperature range (e.g. Ames et al. 1983). It was therefore not possible to draw any general conclusions from the available studies that are directly relevant to the Gunnedah and Surat Basin.

4.1.5. Integrating attenuation parameters to calculate residual concentration

In order to estimate the residual environmental concentration of a given chemical at a receptor location, attenuation due to transformation (chemical, biological, radioactive) and sorption have been integrated in a single closed-from mathematical expression. A review of available analytical solutions was undertaken and the model best suited for the current study was selected (see Appendix 5 for a summary of the review). The requirements for this model are as follows:

- Closed-form analytical expression allowing easy implementation in spreadsheets such as EXCEL[™].
- Sequential coupled first-order transformation or decay allowing to link multi-species transformation productions.
- Linear equilibrium sorption for each of the multiple species.
- One-dimensional advective transport with three-dimensional dispersion.
- Boundary condition for solute source representative of assumed geometry at aquitard/aquifer interface (initial value problem - IVP), and
- Solutions exist in a rectangular coordinate system.

The mathematical model for calculation of the predicted environmental concentration, C (mg/L), assumes first-order degradation or decay of the source concentration, C_0 (mg/L), based on the chemical's half-life, $t_{1/2}$, according to:

$$C = C_0 e^{-\lambda t} \tag{10}$$

where λ is first-order transformation or decay constant (day⁻¹), and t is time (days). The decay constant is defined as:

$$\lambda = \frac{ln2}{T_{1/2}} \tag{11}$$

where $t_{1/2}$ is chemical half-life (days). Typical hypothetical concentration versus travel time curves are shown in Figure 4-5 for four hypothetical chemicals. The chemical with the shortest half-life (chemical 1 in the example of Figure 4-5) displays the fastest decrease in concentration, while chemical 4 has the largest half-life hence its concentration decrease is the slowest of all. Figure 4-5 also shows that with different exposure pathways correspond different travel times, hence the residual concentration will be different for different pathways as the difference in travel time produces different concentrations according to Equation 10.

Next, geological attenuation or sorption onto organic matter and/or mineral fraction of the sediments is taken into account in estimating the environmental concentration.

As chemicals with retardation factors $R_f > 1$ increase the travel time compared to unretarded chemicals ($R_f = 1$), according to $t_R = R_f \times t$, the effect of retardation is incorporated in Equation (10) as follows:

$$C = C_0 e^{-\lambda R_f t} \tag{12}$$

Biodegradation involves biochemical reactions within the sub-surface environment through which a parent compound is changed or transformed to organic or inorganic end products or via a series of intermediates. It is an important mechanism for the removal of organic compounds in soil (Loehr 1989). Aerobic biotic degradation rates (half-life) and pathways for organic compounds in soils are influenced by many factors including; their initial concentration at the time of release to the environment, the toxicity of a given compound and its daughter compounds, the physical and chemical

properties of the compound in question and the physical, chemical and biological properties of the soil (Scow and Johnson 1997). In the sections below, we briefly present and summarise the previously reported degradation pathways and aerobic and anaerobic biotic degradation half-lives where available, for some of the organic compounds reviewed in this assessment. Bot aerobic and anaerobic degradation rates are considered appropriate in the current assessment involving deeper groundwater and shallow groundwater (in discharge areas).

Biodegradation studies and the parameters derived for modelling (e.g., biodegradation rate) often involve tests in solution culture and batch systems, with experimental conditions often different from those in groundwater. Two important questions arise: (i) whether biodegradation rates measured in solution culture are appropriate to groundwater, and (ii) whether parameters measured in batch systems can be extrapolated to dynamic flow systems such as real groundwater systems. The few comparative studies reported to date suggest differences in kinetic parameters are mainly due to indirect effects (differences in solution chemistry between solution cultures and solutions with soil or sediments present) rather than direct effects of sorbing surfaces on microorganisms (Scow and Johnson 1997). When batch-derived biodegradation parameters are applied to coupled flow and transport systems, mass-transfer limitations may occur which might require correction of the batch-derived parameters (Scow and Johnson 1997). To address these uncertainties around biodegradation parameters, introduced when solution cultures and batch systems are the primary source of degradation tests, we here define a range of parameter values rather than using single values and subsequently run the simulations multiple times (i.e. for minimum, mean, and maximum parameter values).



Figure 4-5 Hypothetical example of chemical concentration as function of travel time in deeper groundwater

When chemicals interact with the soil solid phases (organic carbon, clay, iron oxides), sorption has to be accounted for in the solute transport equation. The sorption process is usually described by means of the retardation factor R_f , defined

through Equation (1) and involves knowledge about the solid density (ρ_s , g/cm³ of solids), and the distribution coefficient for instantaneous, linear and reversible sorption (K_d , L/kg).

4.2. Chemical transformation pathways and half-lives

4.2.1. Conceptual model

In cases where chemicals are consecutively undergoing biodegradation and transformation, the rate of transformation is often described as a first-order process. Especially biodegradation kinetics (the time-dependent substrate removal and metabolism) in soil have conveniently been described by means of relatively simple mathematical models including first-order kinetics (Scow and Johnson 1997). In this case a biodegradation constant μ (days⁻¹) is calculated according to:

$$\mu = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \tag{13}$$

where $t_{1/2}$ is the chemical half-life (days). In case several chemicals are involved in a sequential first-order decay or degradation chain (C_i , i = 1, n):

$$C_1 \to C_2 \to \dots \to C_n \tag{14}$$

a set of coupled differential equations governing advection-dispersion, linear-equilibrium transport of a sequence of solutes consecutively undergoing biodegradation and transformation will be invoked. For two elements, C_1 and C_2 , the coupled advection-dispersion equilibrium partitioning – first-order biodegradation equation becomes (van Genuchten 1985):

$$\frac{\partial R_{f1} \theta C_1}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial C_1}{\partial x} \right) - \frac{\partial q C_1}{\partial x} - \mu_1 R_{f1} C_1$$
(15)

$$\frac{\partial R_{f2} \partial C_2}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial C_2}{\partial x} \right) - \frac{\partial q C_2}{\partial x} - \mu_2 R_{f2} C_2 + \mu_1 R_{f1} C_1$$
(16)

where R_{f_1} and R_{f_2} are retardation factors for chemical C_1 and C_2 , respectively and μ_1 and μ_2 are first-order biodegradation constants for chemical C_1 and C_2 , respectively.

4.2.2. Chemical-specific transformation pathways

Transformation pathways and rates (or half-lives) are discussed for all organic compounds. The majority of laboratory and field data is available for aerobic conditions, typical of soil and shallow groundwater. For a few compounds half-lives were available for anaerobic conditions, typical of deeper groundwater.

4.2.2.1. 2-methylphenol

Ahamad et al. (2001) summarised literature reported metabolic pathways for 2-methylphenol or o-cresol degradation by *Pseudomonas* in soil (see Figure 4-6). O-cresol initially degrades to 3-methylcatechol and subsequently degrades to form 2-hydroxy-6 ketohepta-2,4 dieonate, followed by 2-ketopent-4-eonate and 4-hydroxy-2-ketopentanoate. Degradation studies of o-cresol in agricultural soils Loehr (1989) determined half-lives ranging between 1.6 to 5.1 days. Similar to the other phenolic compounds discussed here, reported degradation rates appear to have been influenced by their initial

concentration in soil, the pH of the soil and factors including cation exchange capacity (CEC) and organic carbon content of the test soils.

Aronson and Howard (1998) recommend a lower-limit half-life of 20 days (the sole reported field study) and an upper limit half-life of 1386 days for anaerobic conditions.



2-hydroxyl-6 ketohepta-2,4-dienoate(enol)

Figure 4-6 Summary of reported metabolic degradation pathway for o-cresol (based on Ahamad et al. 2001).

4.2.2.2. Naphthalene

Naphthalene has been the subject of numerous degradation studies where bacteria in soil have degraded naphthalene to compounds such as naphthalene diol, salicylic acid, and catechol. Some pure culture studies have shown bacteria utilise naphthalene as a source of carbon (Treccani et al. 1954), whilst others have emphasised the ability of fungi to oxidise naphthalene (Cerniglia 1984). Oxidation pathways for culture conditions published in Cerniglia (1984) include five metabolites of naphthalene along the degradation pathway: cis-1,2-dihydroxy-1,2-dihydronaphthalene, 1,2-dihydroxynaphthalene, cis-o-hydroxybenzalpyruvic acid, salicylic acid, and catechol (Figure 4-7). Biodegradation has been shown to remove naphthalene from soil, with an estimated half-life ranging from 2.1 days in a sandy loam soil (Park et al. 1990) to more than 88 days in pristine sediments (Herbes and Schwall 1978).

Under anaerobic conditions the recommended half-life range is from 96 days (the mean value for the entire field/in situ microcosm data set) to not biodegradable anaerobically (i.e. zero degradation rate) (Aronson and Howard 1998).

Naphthalene is very toxic to aquatic organisms, with PNEC¹⁷ values of 2.4 μ g/L (EC 2003). As far as human health is concerned, combined exposure may result in haemolytic anaemia, inhalation toxicity and carcinogenicity (EC 2003).

¹⁷ a 99% species protection value for pristine waters (moderate reliability)



Figure 4-7 Proposed catabolic pathway for naphthalene by soil bacteria (based on Denome et al. 1993; Kiyohara et al. 1994; Goyal and Zylastra 1997).

4.2.2.3. 2-butoxyethanol

Degradation studies of 2-butoxyethanol have received little attention in the literature and therefore a paucity of data exists. A review of the toxicological profile for 2-butoxyethanol by ATSDR (1998) did not identify any studies that report degradation products or known pathways. Hydrolysis of 2-butoxyethanol is unlikely, as it contains both alcohol and ether functional groups, which are generally resistant to hydrolysis (Harris 1990). Aerobic biodegradation studies of 2-butoxyethanol using sewage for inocula and mineralisation (of the compound to carbon dioxide and water) as a measure of biodegradation indicated, 5% mineralisation in 5 days (DOW 1993), 57-74% in 10 days (DOW 1993; Price et al. 1974), and 72-88% in 20 days (DOW 1993; Price et al. 1974). Waggy et al. (1994) determined the biodegradation of 2-butoxyethanol to be 47% in 5 days, 70% in 15 days and 75% in 28 days, using a closed bottle test with settled sewage as a microbial inoculum. Based on these test procedures, all studies indicate that 2-butoxyethanol is readily biodegradable.

The aerobic biodegradation half-life of 2-butoxyethanol in surface water has been estimated by Howard et al. (1991) to range between 7-28 days. The aerobic biodegradation half-life in groundwater has been estimated to range from 14 to 56 days (or 8 weeks) (Howard et al. 1991). An aerobic biodegradation half-life was also estimated as part of this assessment to be 17.33 days (~416 hours) using BIOWIN (US EPA 2012b). However, as the availability of oxygen decreases with the increase in depth of soil or sediment, the rate of aerobic biotransformation decreases. As a result, this compound may persist longer in deeper soils and sediments.

The aqueous and soil anaerobic biodegradation half-life was estimated to range from 28 to 112 days (or 16 weeks) (Howard et al. 1991; ATSDR 1998).

By invoking analogy to animal metabolism, 2-butoxyethanol may undergo enzymatic oxidation (e.g. via dehydrogenase) to 2-butoxyacetylaldehyde, then to 2-butoxyacetic acid and finally to CO_2 and water (ATSDR 1998).



Figure 4-8 Enzymatic oxidation of 2-butoxyethanol (based on ATSDR 1998).

4.2.2.4. Bronopol

Bronopol, one of many possibly biocides, are essential components of hydraulic fracturing fluids used for unconventional gas extraction. Within the well environment, bacteria may cause bioclogging and inhibit gas extraction, produce toxic hydrogen sulfide, and induce corrosion leading to downhole equipment failure. Kahrilas et al. (2014) found that:

- uncharged biocides will dominate in the aqueous phase and be subject to degradation and transport whereas charged biocides will sorb to solids and be less bioavailable,
- many biocides are short-lived or degradable through abiotic and biotic processes, while some may transform into more toxic or persistent compounds,
- understanding of biocides' fate under typical downhole conditions of high pressure, temperature, and salt and
 organic matter concentrations is limited.

Bronopol can be stable to hydrolysis under normal/ambient conditions, but susceptible to hydrolysis when exposed to elevated temperatures and alkaline conditions (US EPA 1995b). Degradation pathways for bronopol vary depending on the environmental conditions and medium. Bronopol has been found to degrade (hydrolyse) to formaldehyde, 2-hydroxymethyl-2-nitropropane-1,3-diol (tris) and 2-bromo-2-nitroethanol (BNE) in a review summarised by the United States Environmental Protection Agency (US EPA 1995b). Other degradation products have been reported and include bromonitromethane (BNM) and nitromethane (NM) (Figure 4-9; Cui et al., 2011), bromo-nitroethane, bromo-ethanol, and bromo-nitroethanol (Wang et al. 2002).

In ambient laboratory conditions, the half-life for bronopol due to hydrolysis was determined to be approximately 6,570 days (or 18 years) at pH 4, about 548 days (or 1.5 years) at pH 6 and about 61 days (or 2 months) at pH 8. At higher temperatures, hydrolysis is greatly accelerated. At an elevated temperature of 60°C and a pH of 4 and 8, half-lives were found to be much shorter, 4 and 0.125 days (or 3 hours), respectively (US EPA 1995b). For the purpose of this study, it was assumed that bronopol will degrade to formaldehyde.



Figure 4-9 Proposed degradation pathways for bronopol in natural waters (based on Cui et al. 2011).

4.2.2.5. Limonene

Similar to 2-butoxyethanol, limonene does not have functional groups for hydrolysis, its cyclohexene ring and ethylene group are known to be resistant to hydrolysis and it therefore is an unlikely process in terrestrial or aquatic environments (US EPA 1994b). Biotic degradation of limonene by some species of microorganisms has been reported. For example, *Penicillium digitatum, Corynespora cassiicola and Diplodia gossypina* (Abraham et al. 1985), and a soil strain of *Pseudomonas* sp. (PL strain) (Dhavalikar and Bhattacharayya 1966; Shulka and Bhattacharayya 1968). MITI (1992) demonstrated that limonene was readily biodegradable with 41–98% degradation by biochemical oxygen demand in 14 days; testing was under aerobic conditions in a standard test specified by the OECD (OECD 1981). An overview of microbial strains found to be capable of bioconversion of limonene yielding a mixture of oxidation products is available from Mikami (1988). Based on three pathways, the degradation products identified were carveol, perillyl alcohol, and limonene epoxide (Mikami 1988). A more recent review of biodegradation products is available from Duetz et al. (2001).

While biodegradation occurs under aerobic conditions, it does not seem to occur under anaerobic conditions (WHO 1998b).



Figure 4-10 Biodegradation pathways for d-limonene by a Pseudomonad. Pathway 1 (P-1), pathway 2(P-2), pathway 3 (P-3), limonene (1), carveol (2), carvone (3), perillyl alcohol (4), limonene epoxide (5), dihydrocarvone (6) (based on Mikami 1988).

4.2.2.6. HMX

HMX has a relatively low affinity for particulate matter, with a correspondingly low log K_{OC} (~1-2) (Sharma et al. 2013). Sorption of HMX can be enhanced where there is a higher amount of organic matter, while having multiple nitro functional means an increasing clay content can also enhance its extent of sorption, although this effect is expected to be minimal (Monteil-Rivera et al. 2003; Sharma et al. 2013). Despite its low water solubility (5 mg/L), the mobility of HMX is therefore expected to be high in terrestrial environments (TOXNET). HMX is reasonably stable to biodegradation (Pennington and Brannon 2002) and abiotic degradation, although some degradation (<10%) can occur at very high pH (12) and elevated temperature (50°C), with degradation products including 4-NDAB (2,4-diazabutanal), NO₂ ⁻, N₂O, N₂, and formaldehyde, in common with other cyclic nitramine explosives (Balakrishnan et al. 2003, Monteil-Rivera et al. 2003).

In the case of cyclic nitramines, such as HMX and RDX, once an initial change/attack by fungus, bacteria or other microorganisms occurs, the molecule becomes unstable and undergoes spontaneous decomposition that may be nonenzymatic and ultimately procudes N₂O and CO₂. In other words, HMX is believed to mineralise without production of intermediate metabolites. There is indeed considerable experimental evidence that N₂O is the main product from both aerobic and anaerobic biodegradation of RMX, and likely also of HMX. It is further believed that during the biodegradation of cyclic nitramines unstable intermediates are formed that also spontaneously decomposed to N₂O and CO₂ (Hawari et al. 2000). Using a strictly aerobic symbiotic bacterium culture, Van Aken et al. (2004) measured HMX biotransformation yielding a half-life of approximately 15 days.

Anaerobic degradation has mainly been observed in sludge solutions, with some studies reporting biodegradation in soils. Using domestic anaerobic sludge, Hawari et al. (2001) measured HMX biotransformation yielding a half-life of approximately 2.3 days (presence or absence of glucose did not influence the half-life) (Figure 4-11).



Figure 4-11 Potential biodegradation routes of HMX during treatment with anaerobic sludge. Path b: Ring cleavage followed by competing chemical and biochemical transformations. A square bracket indicates unidentified product whereas a question mark indicates potential presence that requires further experimental verification (based on Hawari et al. 2001).

4.2.2.7. Methylchloroisothiazolinone

Methylchloroisothiazolinone (MCI) has a very high water solubility and low log K_{OC} (1.5-2.2) which suggests a high mobility is likely in the soil environment (US EPA 1998b). It is stable to hydrolysis at low to neutral pH but is susceptible to alkaline hydrolysis, with a half-life of 22 days at pH 9 (25°C) (US EPA 1998b).

MCl was found to be readily degradable in a sandy loam soil (pH 4.9) under aerobic conditions (half-life of 0.21 days or 5 hours). Because of the low adsorption coefficient (K_d = 0.1 - 4.9 L/kg or K_{OC} = 30 - 310), the chemical is expected to be very mobile in soil (US EPA 1998b).
There is evidence for MCI biodegrading under anaerobic conditions, with a half-life of 5 days in river sediment (Jacobson and Williams 2000).



Figure 4-12 MCI biodegradation under anaerobic conditions (based on Jacobson and Williams 2000).

4.2.2.8. Acrylamide polymer

Pure polyacrylamides are nontoxic, relatively stable to a variety of reaction conditions, and, most critically, do not undergo unzipping type reactions to form significant amounts of the neurotoxic acrylamide. Acrylamide has been classified by the US EPA as a Group B2 probable carcinogen. Degradation pathways of polyacrylamides were reviewed by Caulfield et al. (2002). These include thermal, photochemical, biological, chemical, and mechanical degradation, where the degradation chemistry is dominated by the reactivity of the substituent amide group. For example, photodegradation has been shown to degrade the polymer backbone into monomers. Microbial enzymes have been shown to facilitate biological hydrolysis of polyacrylamides into ammonia and an acid (Caulfield et al. 2002).

Polyacrylamide in its pure form has been found to be thermally stable below 200°C and resistant to biodegradation, while mechanical degradation of the polymer is likely to be a major fate pathway in the environment (Seybold 1994, Caulfield et al. 2002). pH-dependent hydrolysis of polyacrylamide can occur through conversion of polyacrylamide to acrylic acid at acidic and basic pH values, although the rate is highly dependent on the degree of acrylic acid already present within the polymer (Muller et al. 1980, Zurimendi et al. 1984, Caulfield et al. 2002). In the case of Muller et al. (1980), tests were done at 100 °C. Sorption of hydrolysed (acrylic acid-containing) polyacrylamide can occur mainly with clays, although the degree of sorption is highly dependent on the extent of acrylic acid within the polymer structure (Seybold 1994). Polyacrylamide has a very high water solubility and, combined anionic nature, suggests that polyacrylamide is expected to be highly mobile in a soil environment (Caulfield et al. 2002, TOXNET), although polyacrylamide may irreversibly adsorb to soils under dry conditions.

4.2.3. Summary of chemical half-life parameters

Due to the assumed low levels of organic carbon in all aquifers except the Namoi and Dawson River alluvium, it was assumed that abiotic degradation via hydrolysis would be the dominant degradation process. However, most of the organic chemicals selected do not have functional groups susceptible to hydrolysis, although bronopol and methylchloroisothiazolinone have been reported to degrade abiotically under alkaline conditions (US EPA 1995b, 1998a). HMX was shown to hydrolyse under both fresh and saline conditions (Brannon et al. 2005).

Abiotic degradation processes are expected to increase proportionally with temperature so that an increasing temperature will lead to an increase in hydrolysis rates, which can often be dramatic. For example, the half-life of bronopol at 20°C (pH 8) is around 60 days, while at 60°C it is 0.125 days (or 3 hours) (US EPA 1995b). Bronopol would therefore not be expected to remain stable under the conditions experienced in the deeper formations (high temperature and pH >7). The hydrolysis half-life of methylchloroisothiazolinone is considerably shorter at pH 9 (22 days at 25°C) than for bronopol and it, too, would be expected to have a short half-life under elevated temperatures experienced within the deeper formations.

A summary of the half-life parameters is provided in Table 4-4, while details of their derivation are available from Appendix 5. Due to the paucity of experimental degradation data, chemical half-life was also estimated using the EPI Suite BIOWIN

model (US EPA 2012b). BIOWIN provides the user with half-lives in categories of hours, days, weeks, or months. These broad classes were converted into unique numerical half-life value using the conversions from Table 4-3. The following abstract from the EPI Suite BIOWIN model briefly summarised the methodology in regards to Table 4-3:

"These two models estimate the time required for "complete" ultimate [Biowin3] and primary [Biowin4] biodegradation. Primary biodegradation is the transformation of a parent compound to an initial metabolite. Ultimate biodegradation is the transformation of a parent compound to carbon dioxide and water, mineral oxides of any other elements present in the test compound, and new cell material. The models are based upon a survey of 17 biodegradation experts conducted by EPA, in which the experts were asked to evaluate 200 compounds in terms of the time required to achieve ultimate and primary biodegradation in a typical or "evaluative" aquatic environment (*Boethling et al. 1994*). This survey followed a similar survey for 50 compounds, described by Boethling and Sabljic (1989). In the second survey, each expert rated the ultimate and primary biodegradation of each compound on a scale of 1 to 5. The ratings correspond to the following time units: 5 - hours; 4 - days; 3 - weeks; 2 - months; 1 - longer. It should be noted that the ratings are only semi-quantitative and are not half-lives. Thus for example if the averaged expert rating for ultimate degradation of a compound is 2.5, it means the experts considered that the compound would biodegrade completely in a time frame somewhere between "a matter of weeks" and "a matter of months", with no exact time or half-life being applied."

No. of compounds ^d	BIOWIN3/4	BIOWIN3/4 category		Experimental half-lives (days)			
	Descriptor	Model output ^e	Range	Median	Mean	10% Trimmed mean	- water half-life (days)ª
0	Hours	> 4.75	_	-	_	_	0.17
0	Hours-days	4.25-4.75	-	_	-	_	1.25
0	Days	3.75-4.25	-	_	-	_	2.33
13	Days-weeks	3.25-3.75	0.13—26	4.65	7.30	6.25	8.67
74	Weeks	2.75-3.25	0.41—567	8.35	26.4	12.4	15
78	Weeks-months	2.25-2.75	0.3—1720	14.9	112 ^b	37.6	37.5
44	Months	1.75-2.25	1—1420	85	187	126	60 (120)
19	Recalcitrant	<1.75	5.6—3800	120	508	255	180
11 ^c	_	1.25-1.75	5.6—790	88	190	144	180 (240)
8 ^c	_	<1.25	25.5-3800	281	945	623	180 (720)

Table 4-3 Experimental primary degradation half-lives vs. EPI Suite default half-lives (US EPA 2012b).

^a Numbers in parentheses: suggested revised default half-lives; ^b One outlying observation was deleted: 25,045 days for CAS no. 13029-08-8; ^c Compounds in the 19-compound 'recalcitrant' category were divided into two groups with respect to BIOWIN3 output, as shown; ^d Number of compounds used to estimate biodegradation; ^e Ratings are semi-quantitative and are not half-lives; they are based on expert surveys that rated compound biodegradation on a scale of 1 to 5.

4.3. **Attenuation parameters for organic substances**

4.3.1. Sorption onto organic carbon

Organic carbon is important in binding organic contaminants and, generally, an increase in organic carbon will also lead to an increase in the sorption of organic contaminants. For this reason, measured liquid-solid partition coefficient (K_d) values are generally normalised to the fraction of organic carbon (f_{OC}) within a solid matrix, such that $K_{OC} = K_d / f_{OC}$ (f_{OC} = fraction of organic carbon, g carbon /g solid matrix). Except for the coal bearing formations, most of the layers within the formation in this study were dominated by sandstones, siltstone and mudstone, so the f_{OC} was assumed to be minimal and make a negligible contribution to sorption. The correction factor applied to default K_{OC} values in such cases was therefore 0, i.e. organic carbon was sufficiently low such that it was not expected to have any impact on sorption.

4.3.2. Sorption onto rock matrix

Clays in soils and mineral formations can enhance the sorption of organic chemicals which contain cationic functional groups (e.g. amines and nitro) beyond what is predicted from the fraction of organic carbon. In this case, however, there was no evidence to suggest that the sorption of organic substances such as HMX or bronopol would be enhanced beyond existing K_{oc} values through the increased proportion of clay in soils (Sharma et al. 2013).

4.3.3. Default sorption (K_d and K_{oc}) and degradation (half-life) values

Default K_{OC} (organic substances) and degradation (half-life) values were compiled from the literature (Table 4-4). Details about derivation of K_{OC} (and half-life) values are provided in Appendix 5.

No	Substance name	CAS	Log[K _{oc} (L/kg)]	Half-life (days)		(days)
		Number		Anaerobic	Aerobic	Hydrolysis
1	2-methylphenol (o-cresol)	95-48-7	1.34 – 2.39	20-1,386	1.6-5.1	n.a.
2	Naphthalene	91-20-3	1.23 - 4.43	96 – nbd	2.1-88	n.a.
3	Limonene	138-86-3	3.00 - 4.77	n.a.	2.3-18	n.a.
4	НМХ	2691-41-0	1.50 - 3.10	2.3	15	21.1-31.2
5	2-butoxyethanol	111-76-2	0.46 - 0.90	28-112	7-28#	n.a.
					14-56 ^{\$}	
6	Bronopol	52-51-7	-0.03 – 3.15	n.d.	n.d.	At 20 °C: 18y (pH4), 1.5y (pH6), 2 months (pH8); At 60°C: 4days (pH4), 3h (pH8) 0.094-0.13 (surface waters, pH 7.4-7.7)

Table 4-4 Summary of default sorption and degradation parameters (minimum – maximum value). n.a = not applicable; n.d. = not data; nbd = not biodegradable (based on Appendix 5).

7	Methyl-chloro- isothiazolinone (MCI)	26172-55-4	1.48 - 2.16	5	0.21	22 (pH9, 25°C)
8	Acrylamide polymer	9003-05-8	1.40 - 2.60	n.d.	n.d.	n.a. (likely inert)

[#] surface water; ^{\$} groundwater

4.3.3.1. Adaptation of K_{oc} and half-life values for organic substances

The effective value of the attenuation parameters to be used in the model will be determined as a product of a default value from literature and the scaling factor assigned for a particular geological layer in question. A scaling factor for each geological formation will be established based on the nature of the formation and conditions associated with it. For example, the scaling factor for K_{OC} for an individual geological layer (e.g. sandstone, coal seam) will be based on the type and contents of organic carbon and mineral matter as well as pH, EC and temperature. For coal seams (being highly carbonaceous) a scaling factor > 1.0 may need to be used to allow enhanced sorptivity by coals especially under saline conditions, whereas for a sandstone (which is devoid of organic carbon and may have an alkaline pH) a scaling factor < 1.0 may be assigned (i.e. reduced sorption relative to the default value).

The literature value of half-life will similarly be adapted based on the redox state (aerobic or anaerobic), ambient temperature of the formation and its likely microbial status. Coal seams may be expected to support some microbial activity whereas a sandstone may essentially be devoid of microbial activity. The positive or negative effect of temperature on rate of degradation will be taken into account in assigning the scaling factor for a geological formation. Certain compounds that are not expected to degrade under anaerobic conditions may be assigned zero degradation rates in relevant geological layers during model simulations.

4.3.3.1.1. Gunnedah Basin

In the Namoi alluvium layer, the mean soil organic carbon at the soil surface was assumed to be ~1% (Ward 1999). This was expected to be the case until a depth of 1 m where soil organic carbon was expected to have decreased to 10% of the value at the soil surface, or 0.1% organic carbon. The value of 0.1% organic carbon is assumed to be appropriate for the Namoi alluvium. Alluvial plains soils can contain a mean clay content of 44% (Ward 1999). Clay in soils can enhance the sorption of organic chemicals which contain cationic functional groups (e.g. amines and nitro) beyond what is predicted from f_{OC} . In this case, however, there was no evidence to suggest that the sorption of HMX or bronopol (both contain cationic functional groups) would be enhanced through the presence of clay in soils (Sharma et al. 2013).

The Pilliga Sandstone and Upper and Lower Maules Creek formation are assumed to have a negligible organic carbon content (see Section 4.1.1). The parameter f_{oc} is therefore zero for all these layers.

Shales and siltstones of the Blythesdale Group are assumed to have some organic carbon (see Section 4.1.1), based on an average of 0.8 % TOC for shale and 10% shale in the formation (i.e. %OC = 0.08 or f_{OC} = 0.0008).

Organic carbon was assumed to be very high (55%) within the coal seams (Hoskisson and Maules Creek-Bohena), with half of the depth of the seam being composed of coal (see Section 4.1.1), yielding a scaling factor of 0.5; the OC values were adjusted accordingly, i.e. the adjusted or rescaled $f_{OC_r} = 0.5 \times 0.55 = 0.275$. For reasons of consistency the parameter f_{OC_r} will also be used for the other non-coal bearing formations, the difference being that the scaling factor for these formations is assumed to be 1 as the organic matter is assumed to be uniformly distributed across the entire formation (i.e. $f_{OC_r} = 1 \times f_{OC}$).

With coal being a highly carbonaceous material with a high surface area, sorption of most organic compounds to coals on per unit mass basis is expected to be higher than that in soil organic matter (Simane et al. 2016). This adjustment factor

could potentially be higher for naphthalene, HMX and limonene, due to their low water solubilities and the relatively high TDS leading to a "salting out" effect. Since this effect is concentration dependent for each chemical, however, an adjustment factor higher than that applied to the other chemicals was not given. Adjusted f_{OC_r} and half-life values for organic substances are given in Table 4-5.

Table 4-5 Table of fate parameters adjusted for Gunnedah basin geology (organic chemicals). A = 2-methylphenol, B = Naphthalene, C = d-Limonene; D = HMX,
E = 2-butoxyethanol, F = Bronopol, G = Methylchloroisothiazolinone, H = Acrylamide polymer. # Multiply default Koc by the factor foc_r (fraction of organic
carbon × scaling factor); a factor of 0 implies extent of sorption essentially approaching 0. Value given is worst case of known abiotic or biotic degradation.
Biotic degradation assumed to be minimal where minimal %OC; @ "Salting out" likely to decrease water solubility – dependent on concentration of species i.e.
approaching water solubility; and Assume conditions as per Pilliga sandstone. NBD = not biodegradable; ND = No Data.

Geology	Ogy OC (%) and f_{OC_r} # (g/g) Adjusted half-life (days)								
8/		А	В	С	D	E	F	G	Н
Namoi alluvium	$OC = 0.1; f_{OC_r} = 0.001$	5.1	88	18	31.2	56	60	22	ND
	(A, B, C, D, E, F, G)								
Pilliga	$OC = 0; f_{OC_r} = 0$	1,386	NBD	NBD	31.2	112	60	22	ND
Sandstone	(A, B, C, D, E, F, G)								
Blythesdale	$OC = 0.08; f_{OC_r} = 0.0008$	1,386	NBD	NBD	31.2	112	60	22	ND
Group	(A, B, C, D, E, F, G)								
Hoskisson seam	OC = 55.5; <i>f</i> _{OC_r} = 0.275	1,386	NBD	NBD	31.2	112	60	22	ND
	(A, D, E, F)								
	>27.5 (B, C, G) [@]								
Maules Creek	$OC = 0; f_{OC_r} = 0$	1,386	NBD	NBD	31.2	112	60	22	ND
Formation (upper)	(A, B, C, D, E, F, G)								
Maules Creek	OC = 55.5; <i>f</i> _{OC_r} = 0.275	1,386	NBD	NBD	31.2	112	60	22	ND
Formation (Bohena coal	(A, B, C, D, E, F, G)								
measures)									
Maules Creek	$OC = 0; f_{OC_r} = 0$	1,386	NBD	NBD	31.2	112	60	22	ND
Formation (lower)	(A, B, C, D, E, F, G)								

4.3.3.1.2. Surat Basin

For the Dawson River alluvium a value of 0.1% organic carbon is assumed to be appropriate, based on the reasoning developed for the Namoi alluvium.

The BMO Group, Westbourne, Springbok and Hutton Sandstone are all assumed to have a negligible organic carbon content. The parameter f_{OC} is therefore zero for all these layers.

Gubberamunda Sandstone is considered to have similar characteristics as the Blythesdale Group, as far as organic carbon is assumed. Based on an average of 0.8 % TOC for shale and 10% shale in the formation, the parameter f_{OC} = 0.0008.

Organic carbon was assumed to be very high within the coal seams, i.e. 31.5% (Walloon Coal Measures), with on average 15 m of net coal thickness for an average formation thickness of 375 (see Section 4.1.2), yielding a scaling factor of 15/375

= 0.04; the OC values were adjusted accordingly, i.e. the adjusted $f_{OC_r} = 0.04 \times 0.31.5 = 0.0126$. Geology-specific value for f_{OC_r} and half-life for organic substances are given in Table 4-7.

Geology	OC (%) and			A	djusted half	f-life (days)			
	f _{oc_r} # (g/g)	А	В	С	D	E	F	G	Н
Dawson River alluvium	OC = 0.1; f _{OC_r} = 0.001	5.1	88	31.2	56	60	5.1	88	31.2
	(A, B, C, D, E, F, G)								
Bungil	OC = 0; <i>f</i> _{OC_r} =		22	18	ND			22	18
Formation-	0								
Mooga Sandstone-	(A, B, C, D, E,								
Orallo	F, G)								
Formation									
(BMO Group)									
Gubberamunda	OC = 0.08;	1,386	NBD	31.2	112	60	1386	NBD	31.2
Sandstone	<i>f</i> _{OC_r} = 0.0008								
	(A, B, C, D, E,								
	F, G)								
Westbourne	OC = 0; <i>f</i> _{OC_r} =		22	NBD	ND			22	NBD
Formation	0								
	(A, D, E, F)								
	>27.5 (B, C,								
	G) [@]								
Springbok	OC = 0; <i>f</i> _{OC_r} =	1,386	NBD	31.2	112	60	1,386	NBD	31.2
Sandstone	0								
	(A, B, C, D, E,								
	F, G)								
Walloon Coal	OC = 31.5;		22	NBD	ND			22	NBD
Measures	<i>f</i> _{OC_r} = 0.0126								
	(A, B, C, D, E,								
	F, G)								
Hutton	OC = 0; f _{OC_r} =	1,386	NBD	31.2	112	60	1,386	NBD	31.2
Sandstone	0								
	(A, B, C, D, E, F, G)								

Table 4-6 Table of fate parameters adjusted for Surat Basin geology (organic chemicals). A = 2-methylphenol, B = Naphthalene, C = HMX, D = 2-butoxyethanol, E = Bronopol, F = Methylchloroisothiazolinone, G = d-Limonene, H = Acrylamide polymer. # Multiply default K_{OC} by $f_{OC_{-}r}$ (fraction of organic carbon × scaling factor); a factor of 0 implies extent of sorption essentially approaching 0. Value given is worst case of known abiotic or biotic degradation. Biotic degradation assumed to be minimal where minimal $\%OC_r @$ "Salting out" likely to decrease water solubility – dependent on concentration of species i.e. approaching water solubility; and Assume conditions as per Pilliga sandstone.

4.4. Attenuation parameters for inorganic substances

Selection of partition coefficients (K_d) for inorganic substances in deep groundwater matrices was undertaken. Partition coefficient (K_d) values were sought for arsenic, boron, barium and uranium. It is important to note that these elements are persistent inorganic chemicals that do not undergo degradation (biotic or abiotic) in the same manner as organic chemicals. The exception is uranium, which is a radionuclide with a specific half-life depending on the isotope. For the most abundant isotope ²³⁸U the half-life is 4.47×10^9 years; because of this very long half-life, very little decay of ²³⁸U will happen even in several thousand years. Consequently, half-lives are not a relevant parameter for these chemicals. Adsorption, whereby these substances adsorb onto rock surfaces, sediments and soils is one of the most important processes attenuating groundwater concentrations.

A literature survey was conducted using Google and Web of Science. Most of the literature found related to the determination of K_d values for soils or alluvial sediments obtained from shallow depths. There was little K_d data for hard rocks particularly of those matching the geological description of the Namoi or Surat strata. Surprisingly, given international concerns on groundwater contamination, there was only very limited data for arsenic adsorption onto rocks and soils. Only a few studies have compared the relative adsorptive affinities of As(III) and As(V) (Dixit and Hering 2003).

A number of physico-chemical factors are likely to influence sediment-water partitioning in deep groundwater systems such as pH, groundwater composition, temperature and solid phase composition (Table 4-7). Initially, it was intended to develop scaling factors that allowed adjustment of K_d for these factors. However, this was not possible owing to the lack of established relationships between K_d and the variables in question.

In reality, the pH variability observed in groundwater from the Gunnedah and Surat Basins is not that great. As indicated in Table 4-1 and Table 4-2, the median pH of the groundwater associated with the target coal seam formations varies from 7.6 (Gunnedah) to 8 (Surat). The geothermal gradient is quite significant (section 4.1.1.2) and water temperature ranges from 20°C in surface strata to a maximum of 58°C at depth. There is insufficient geochemical information on the Namoi and Surat strata that can further inform the selection of K_d values for the elements in question (i.e redox potential, detailed mineral composition, groundwater composition).

In view of the sparsity of appropriate data, the following selection criteria were applied in selecting K_d values from literature:

- *K*_d values determined for rocks were preferred over soil and alluvial sediment data.
- If no K_d rock data available then use alluvial sediments data or, as a last resort, soil data.
- Where there is a range of K_d values, the lower values were selected (i.e. underestimate K_d rather than overestimate K_d)
- Select K_d values determined at pH values of between 7 and 9.
- Avoid pure mineral phases such as goethite and other iron minerals as they will overestimate K_d for elements such as As and U.
- Avoid K_d data derived for quartz, as owing to its relative inertness, it likely to provide underestimates of K_d.
- Where there is sufficient data, select an upper and lower bound K_d value.

Default K_d (inorganic substances) values were compiled from the literature (Table 4-8). Note that it was not possible to select different K_d values for each stratum.

Table 4-7 Effect of various physicochemical variables on K_d .

Variable	Effect on K _d
рН	Complex interaction as pH governs the surface charge of mineral surfaces as well as influencing the speciation of elements in solution. In acidic solutions protons will also compete for binding sites. In alkaline solutions, hydroxyl and carbonate ions will form stable complexes with the inorganic elements and thus decrease sorption.
Hardness (sum of the ions which can precipitate as 'hard particles' from water. Sum of Ca ²⁺ and Mg ²⁺ , and sometimes Fe ²⁺) (Appelo and Postma 2004)	For elements where electrostatic adsorption is important (e.g. Ba), Ca and Mg will compete with ions for binding sites. For these elements, <i>K</i> _d is expected to be lower in high hardness solutions.
Solid phase composition	Critically important. Some elements such as As and U undergo chemisorption and form strong surface complexes with iron and manganese containing minerals.
Redox potential	Complex interaction. Redox potential will affect both mineral phase composition and speciation of redox sensitive elements such as As and U.
Temperature	For elements where adsorption is an exothermic process, K_d will decrease as temperature increases. For elements where adsorption is an endothermic process, K_d will increase as temperature increases.
Dissolved carbonate concentration	For elements that form soluble carbonate complexes (e.g. U), K_d will be lower in carbonate containing solutions.
Dissolved organic matter concentration (DOM)	For elements that form soluble complexes with DOM (e.g. U), K_d will be lower in the presence of DOM

Table 4-8 Summary of default sorption parameters for inorganic chemicals.

No	Substance name	CAS Number	K _d (L/kg)	Source
1	Boron (Boric acid, Borax)	10043-35-3, 1303-96-4	0.03 - 0.22	Lower and upper values from Broerman et al. (1997).
2	Uranium	7440-61-1	5 – 5,000	Lower and upper limit based values on available data for crystalline rock samples (US EPA 1999a).
3	Barium	7440-39-3	100 [#] 0.2-0.6 [@] 164*	 # Recommended value for soils (Lintott and Tindall 2007). [@]Hard rock K_d values from diffusion experiments using granitic rocks and minerals (Muuri 2015). *Erdal et al. (1979) reported batch sorption K_d on granite of 164 L/kg at 22 °C and 718 L/kg at 70 °C.
4	Arsenic	7440-38-2	2.90 - 17.3	Lower and upper values for As(V) for Cornish siltstone (Adey 2005).

4.4.1.1. Adaptation of K_d values for inorganic substances

Adjusted K_d values for inorganic substances are given in Table 4-9 for Gunnedah Basin and Table 4-10 for Surat Basin. Due to lack of hydrochemical and mineralogical data, no adjustments of the default values have been made.

Geology	As <i>K</i> d (L/Kg)	B <i>K</i> d (L/Kg)	Ba <i>K</i> d (L/Kg)	U <i>K</i> d (L/Kg)
Namoi alluvium	2.9 - 17.3	0.03 - 0.22	0.2 - 164	5 – 5,000
Pilliga sandstone	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Blythesdale Group	2.9 - 17.3	0.03 - 0.22	0.2 - 164	5 – 5,000
Hoskisson seam / Bohena seam	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Maules Creek Formation (upper)	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Maules Creek Formation (coal measures)	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Maules Creek Formation (lower)	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000

Table 4-9 Table of fate parameters adjusted for Gunnedah Basin geology (inorganic chemicals).

Table 4-10 Table of fate parameters adjusted for Surat Basin geology (inorganic chemicals).

Geology	As	В	Ва	U
	K _d (L/Kg)	<i>K</i> _d (L/Kg)	K _d (L/Kg)	<i>K</i> _d (L/Kg)
Dawson River alluvium	2.9 – 17.3	0.03 – 0.22	0.2 – 164	5 – 5,000
Bungil Formation-Mooga Sandstone-Orallo Formation (BMO Group)	2.9 – 17.3	0.03 – 0.22	0.2 – 164	5 – 5,000
Gubberamunda Sandstone	2.9 – 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Westbourne Formation	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Springbok Sandstone	2.9 - 17.3	0.03 - 0.22	0.2 - 164	5 – 5,000
Walloon Coal Measures	2.9 - 17.3	0.03 - 0.22	0.2 – 164	5 – 5,000
Hutton Sandstone	2.9 - 17.3	0.03 - 0.22	0.2 - 164	5 – 5,000

4.5. Interactions between hydraulic fracturing fluids and geogenics

Coal seams are known to contain a number of contaminants that have the potential to be mobilised during hydraulic fracturing activities (Apte et al. 2017b). Mobilisation can occur because some chemicals used in hydraulic fracturing have the potential to release contaminants from the coal seam, through the effects of, for example, chelating agents, acids, surfactants, and solvents. These geogenic contaminants include trace elements (e.g. arsenic, manganese, barium, boron and zinc), radionuclides (e.g. isotopes of radium, thorium, and uranium) and organic contaminants such as hydrocarbons and phenols. Their release into groundwaters surrounding coal seams raises concerns for their potential impacts.

A recent study investigated the release of potential contaminants from selected coal samples representative of coal seams that are currently, or which may in the future, be subject to gas extraction (Apte et al. 2017a). Chemical leach tests were undertaken to simulate interactions between coal and hydraulic fracturing fluid during the fracturing process. The laboratory leaching tests with dilute acid were designed to provide upper bound estimates for the release of geogenic contaminants. These deliberately harsh conditions were considered sufficiently representative of an actual gas extraction operation.

Over 65 trace elements were quantified in the leachate samples. For at least 18 trace elements, measured concentrations exceeded the surface water quality benchmarks for aquatic ecosystem protection: aluminium, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, lead, manganese, nickel, selenium, silver, thallium, uranium, vanadium and zinc. Where water quality guideline values are available a comparison is made with elemental concentrations to demonstrate the effect of attenuation on contaminant concentrations (see Section 5.6.1). Comparisons of this nature are commonly made in screening level risk assessments in order to understand the potential impacts of contaminants on aquatic environments.

4.6. **Toxicity of Chemicals**

In the subsequent sections ecotoxicity and human health hazards for selected chemicals are discussed based on national and international literature. For each chemical the predicted no effect concentrations (PNEC) for the protection of aquatic freshwater biota and drinking water guideline concentrations for Australia will be summarised (where available). The PNEC values will be used in Section 5.6 to derive minimum separation distances between a chemical source and a potential receptor.

4.6.1. 2-methylphenol (o-cresol)

Three isomers of the geogenic chemical cresol exist, 2-methylphenol (*o*-cresol), 3-methylphenol (*m*-cresol), and 4methylphenol (*p*-cresol). Due to their similar properties, the environmental and human health hazards for cresols compounds are occasional reported collectively.

4.6.1.1. Environmental Hazards

The US EPA ECOTOX Database reports aquatic ecotoxicity of *o*-cresol for fish (LC50 5.6-66 mg/L), insects (LC50 46-80 mg/L), midge (LC50 34 mg/L), hydra and cilates (LC/EC50 31-213 mg/L) molluscs (snail LC50 160 mg/L) and worms (24-165 mg/L) (US EPA 2016c). A chronic NOEC of 1 mg/L for *Daphnia magna* was reported by Kühn et al. (1989) and a chronic EC10 of 2.3-4.6 mg/L for the microalga *Scenedesmus subspicatus* (Kühn and Pattard 1990) for p-cresol (the isomer of o-cresol).

The fate, transport and degradation of cresols in aquatic and terrestrial environments is summarised in ATSDR (2008). The biodegradation of cresols occurs under aerobic conditions; even under anaerobic conditions biodegradation should still be an important removal mechanism. The bioaccumulation and bioconcentration of cresols is expected to be small, or insignificant (ATSDR 2008).

4.6.1.2. Human Health Hazards

Brief exposures to cresols in air cause nose and throat irritations (ATSDR 2008). Ingestion of liquids containing cresols cause serious gastrointestinal damage and even death. Contact of cresols to the skin can cause sever skin damage and can also cause death. Comprehensive detail on the effect of cresols on humans, and animals, is summarised in ATSDR (2008).

There is no drinking water guideline for cresols in Australia.

4.6.2. Naphthalene

4.6.2.1. Environmental Hazards

The Australian Water Quality Guideline for the geogenic chemical naphthalene in freshwater is 16 µg/L and, 70 µg/L in marine water (ANZECC/ARMCANZ 2000). Freshwater acute toxicity data includes four fish species (LC50 120-7,900 µg/L), four crustaceans (LC50 2,160-57,520 µg/L), three insects (LC50 27-20,700 µg/L), and a mollusc (LC50 5,000 µg/L). Chronic toxicity data includes two fish (NOEC 450-2,300 µg/L) and a microalga (EC50 5,000 µg/L). Marine acute toxicity data includes four fish (LC50 750-5,300 µg/L), six crustaceans (LC50 850-5,700 µg/L), a mollusc (LC50 57,000 µg/L) and annelids (LC50 3,800 µg/L). Chronic marine toxicity data are available for two fish (NOEC 120-560 µg/L) and a crustacean (NOEC 21 µg/L) (ANZECC/ARMCANZ 2000). CCME (1999a) also summarise ecotoxicity data for freshwater and marine organisms and report a Canadian interim water quality guideline for naphthalene in freshwater of 1.1 µg/L, and 1.4 µg/L in marine water.

Sediment quality guidelines are also reported in Australia with interim guideline values of 160 mg/kg (low) and 2,100 mg/kg (high) (ANZECC/ARMCANZ 2000). Canada also report sediment quality guidelines (34.6 and 391 mg/kg for interim guideline and probable effect levels respectively) (CCME 1999b).

The fate and behaviour of PAHs in aquatic systems is influenced by a number of physical, chemical and biological processes including; photo-oxidation, hydrolysis, biotransformation, biodegradation and mineralisation. Such processes result in the transformation of PAHs into other substances; adsorption, desorption, solubilisation, volatilisation, resuspension, bioaccumulation and bioconcentration cycle these substances throughout the aquatic environment. These process are described in more detail in CCME (1999b).

Most PAHs are poorly soluble and adsorb strongly to sediment, suspended matter and organic matter (ANZECC/ARMCANZ, 2000). Naphthalene is the most soluble PAH with an octanol-water partition coefficient (K_{ow}) of 3.4 (ANZECC/ARMCANZ, 2000) and has the highest vapour pressure suggesting that volatilisation from the aquatic environment is probably an important removal mechanism.

4.6.2.2. Human health hazards

Naphthalene enters the body by breathing air, drinking water and direct contact with skin. Once in the body, naphthalene will dissolve in blood. Exposure to large amounts of naphthalene causes haemolytic anaemia and may also cause nausea, vomiting, diarrhoea blood in urine and a yellowing of the skin. Most naphthalene leaves the body quickly. There is no direct evidence that naphthalene causes cancer; however, it is considered to be either reasonably anticipated, or, a possible carcinogenic depending on the governing body (ATSDR 2005).

There is no drinking water guideline in Australia for naphthalene. ATSDR (2005) report that the US EPA recommended drinking water contains no more than 100 μ g/L. Naphthalene does not accumulate in food (flesh of animals and fish); however, it may transfer to milk and eggs from cows and hens (respectively) that have been exposed to naphthalene. Occupational exposure should be no more than 500 ppm in air. Above this level naphthalene is immediately dangerous to human health (ATSDR 2005).

4.6.3. Limonene (1-methyl-4-(1-methylethenyl)-cyclohexene)

4.6.3.1. Environmental hazards

No water quality guidelines are reported for the hydraulic fracturing chemical limonene. Toxicity of limonene to aquatic and terrestrial organisms is summarised in WHO (1998b). Aquatic toxicity includes cladocerans (acute EC50 0.42-39 mg/L and chronic NOEC 0.15 mg/L), fish (EC50 0.7-80 mg/L) and insects (LC50 7.7-30.6 mg/L). Terrestrial organisms include insects, a spider worm and birds (dietary exposure).

Based on the physical and chemical properties of limonene, in the aquatic environment limonene is expected to absorb to sediment and suspended matter and to rapidly volatilize to the atmosphere. In groundwater, limonene is expected to have low mobility (WHO 1998). Further details on the environmental transport, distribution and transportation of limonene in the environment can be found in WHO (1998b).

4.6.3.2. Human Health Hazards

Limonene is essentially non-toxic. Upon contact, limonene can react to form small amounts of oxidation products that can cause skin allergy. Contact with limonene or limonene products can cause eye and skin irritation (WHO 1998).

4.6.4. HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)

4.6.4.1. Environmental Hazards

Aquatic ecotoxicity date for HMX is reported in the US EPA ECOTOX Database (US EPA 2016c). Toxicity data include freshwater fish (LC50 15 to >30 mg/L) and midge (EC50 >32 mg/L) with toxicity data also reported for a range of endpoints for cladocerans, microalgae and bluegreen algae (US EPA 2016c).

HMX is relatively stable in the aquatic environment. Neither hydrolysis nor oxidation of HMX in water are expected to be important removal processes. Direct photolysis is probably the primary transformation pathway for HMX in aquatic systems. No data were located regarding HMX transformation in soil or sediment. Based on data for RDX (similar compound to HMX) and HMX transformations in water, microbial degradation does not proceed rapidly and the chemical may be persistent in soil and sediments. No data regarding the bioconcentration potential of HMX were located (ATSDR 1997); however there are some studies on the bioconcentration of HMX in molluscs and fish reported in US EPA (2016c). Bioaccumulation of HMX is not expected to be significant, based on bioconcentration and elimination studies on RDX, an HMX analog, in several species.

4.6.4.2. Human Health Hazards

Information on the adverse health effects of HMX is limited (ATSDR 1997). In one human study, no adverse effects were reported in workers exposed to HMX in air. Animal studies, indicated that exposure to HMX may be harmful to the liver and central nervous system if it is ingested or through dermal contact. The reproductive and developmental effects of HMX have not been well studied in humans or animals. At present, the information needed to determine if HMX causes cancer is insufficient. Due to the lack of information, the US EPA has determined that HMX is not classifiable as to its human carcinogenicity (ATSDR 1997).

4.6.5. 2-butoxyethanol

4.6.5.1. Environmental Hazards

Effects of the hydraulic fracturing chemical 2-butoxyethanol on aquatic biota have been reported for both freshwater and marine/estuarine biota. Despite its high solubility in water, in general the toxicity of 2-butoxyethanol to aquatic biota is low. WHO (1998c) summaries toxicity to freshwater bacteria and protozoan (LOEC = 91 and 700 mg/L to EC50 = >1,000 mg/L), microalgae (LOEC = 35 and 900 mg/L to EC50 = >1,000 mg/L), cladocerans (LC50 = 835 to 5000 mg/L) and fish (LC50 = 165 to >1,000 mg/L). Toxicity to marine and estuarine aquatic biota includes oysters (LC50 = 89 mg/L), shrimp (5.4 to 1,000 mg/L) and fish (116 and 1,250 mg/L). The US EPA (2016c) ECOTOX database also reports toxicity data for a marine amphipod (LC50 = >1,000 mg/L). A predicted no-observed effect concentration (PNEC) of 165 μ g/L for aquatic biota has also been reported (WHO 1998c).

2-butoxyethanol is readily biodegradable in water and not expected to bioaccumulate in aquatic biota (WHO 1998c).

4.6.5.2. Human Health Hazards

The principle human health effects attributed to 2-butoxyethanol exposure have involved the central nervous system, the blood, and the kidneys (ATSDR 1998). In the body, 2-butoxyethanol is converted to metabolites such as 2-butoxyacetic acid. Human exposure to vapours of 2-butoxyethanol have been reported to cause irritation of the nose and eyes, headache, a metallic taste, or vomiting. No effects on blood pressure or pulse nor harmful effects following lung and heart tests were also observed. Ingestion (mainly via cleaning agents) can result in breathing problems, low blood pressure,

lowered levels of haemoglobin, blood in urine and metabolic acidosis. No data identifies 2-butoxyethanol as a cause of reproductive effects, birth defects or cancer in people (ATSDR 1998).

A number of occupational exposure limits have been proposed for 2-butoxyethanol. These include permissible exposure limits (PEL) or recommended exposure limits (REL) of 50 mg/L, 25 mg/L and 5 mg/L depending on the regulating or recommending agency (ATSDR 1998).

4.6.6. Bronopol (2-bromo-2-nitropropane-1,3-diol)

4.6.6.1. Environmental Hazards

Aquatic toxicity of the hydraulic fracturing chemical bronopol has been reported for marine and freshwater biota, and aquatic birds (US EPA 2016d). Microalgae are the most sensitive to bronopol (EC50 = 0.020 - 0.41 mg/L), followed by oysters (EC50 = 0.42 and 0.78 mg/L), water fleas (EC50 = 1.6 mg/L), mysids (LC50 = 4.3 and 5.9 mg/L), duckweed (EC50 = 38 mg/L) and fish (LC50 = 7.5 - 59 mg/L). The exposure of two species of aquatic birds to bronopol via water and dietary exposures result in LC50s of 4,487 and >10,000 mg/L.

Due to bronopol's low octonal/water ratio and high solubility in water, bronopol is not expected to bioaccumulate. Under warm and/or high pH conditions rapid hydrolysis occurs resulting in the formation of formaldehyde which should also be considered in environmental hazard assessments (US EPA 1995).

4.6.6.2. Human Health Hazards

Human health effects of exposure to bronopol are not widely available with toxicological data on bronopol limited to studies using animals. Based on these studies, estimated occupational short and intermediate-term exposure levels and risks to workers have been calculated along with its classification as a Group E chemical, that is, one for which there is evidence of noncarcinogenicity for humans (US EPA 1995).

4.6.7. Methyl-chloro-isothiazolinone (MCI)

4.6.7.1. Environmental Hazards

Limited information is available on the toxicity of the hydraulic fracturing chemical MCI to aquatic biota. Toxicity of a mixture of MCI and methyl-isothiazolinone (MI) was determined for two bacterial species and a ciliate protozoa with EC50 values ranging from 0.063 –0.509 mg/L (Carbajo et al. 2015).

4.6.7.2. Human Health Hazards

Effects of exposure of MCI and MI to animals are reported in CTFA (1992). Human dermal exposure to MCI/MI indicates that it is a skin sensitiser but studies at concentrations of 50 ppm and above are not in agreement (CTFA 1992).

4.6.8. Acrylamide polymer

The hydraulic fracturing chemical acrylamide polymer (or polyacrylamide) is available in anionic, cationic or non-ionic forms and in a variety of molecular weights (chain lengths of the acrylamide monomer).

4.6.8.1. Environmental Hazards

Ecotoxicity data for acrylamide polymer does not appear to exist.

4.6.8.2. Human Health Hazards

Acrylamide polymer is considered to be non-toxic and is used in drinking water treatments for coagulation, flocculation, clarification, filter aid, sludge handling and dewatering. The purity of chemicals used in the treatment of drinking water varies, depending on the manufacturing process. Contaminants may include; acetamide, acetone, acrylamide, acrylic acid, acrylonitrile, copper, hydroquinone, methacrylamide, methyl ether hydroquinone, peroxide, propanamide and sulfate. Unreacted amounts of acrylamide monomer may also be present and this compound is toxic causing peripheral neuropathy and is a probable carcinogen (NRMMC 2011).

A drinking water guideline for acrylamide polymer does not exist in Australia; however, the Australian Drinking Water Guidelines state that contaminants and by-products of acrylamide polymer are not to exceed guideline values (NRMMC 2011).

4.6.9. Boron (Boric acid, Borax)

Boric acid $(B(OH)_3)$ and sodium borates (such as borax, Na₂B₄O₇) predominantly exist in dilute aqueous solutions as undissociated boric acid at a pH of <7; metaborate anion $(B(OH)_4^-)$ becomes the main species in solution at a pH >10. Between pH 6 and 11, and at high concentrations, highly water soluble polyborate ions such as B₃O₃(OH)₄⁻, B₄O₅(OH)₄²⁻ and B₅O₆(OH)₄⁻ are formed. Hence, in natural waters boron primarily exists as undissociated boric acid and some borate ions. For this reason, the chemical and toxicological properties of boric acid and borates are expected to be similar based on equivalent boron concentrations when dissolved in water and at the same pH (WHO 2004b).

4.6.9.1. Environmental Hazards

Boron is an essential nutrient for plants and considered to be a non-essential element for animals, although boron has been found to be beneficial to some animals such as fish (Loewengart 2001) and frogs (Fort et al. 1999).

The current Australian water quality guideline for boron in freshwater is 0.37 mg/L (ANZECC/ARMCANZ 2000); however, some errors were identified in the derivation of this guideline value. Chronic (long-term) toxicity data have been used to derive a revised Australian very high reliability guideline value for boron toxicity to 20 species from 7 taxonomic groups. Revised guideline value of 0.83 mg/L (inclusive of all aquatic organisms) is currently under review by the Department of Agriculture and Water Resources, Australia. This value is comparable to the Canadian guideline value of 1.5 mg/L (CCME 2009), 1.7 mg/L obtained by Dyer (2001) and 1.7 mg/L obtained by Schoderboeck et al. (2011).

There are limited ecotoxicity data available for marine species (two fish species with acute LC50 values of 12.2 and 88.3 mg/L) hence the background boron concentration in seawater (5.1 mg/L) was adopted as a low reliability guideline value in Australia (ANZECC/ARMCANZ 2000).

4.6.9.2. Human Health Hazards

Human exposure to relatively small amounts of boron can occur via water, food (mainly of plant origin) and air; while, exposure to larger quantities can occur through occupational activities. A clear biological function for boron in humans has yet to be identified (IOM 2001; USEPA 2008b).

Boron is rapidly and completely absorbed after ingestion with up to 90% excreted in urine. Following the ingestion of high doses of boron, symptoms include gastrointestinal disturbances, skin eruptions, and central nervous systems stimulation and depression have been reported. Long-term occupational exposure to boron can lead to similar symptoms. There is

evidence to suggest that boron is not mutagenic (NRMMC 2011) and there is no evidence to suggest that boron is carcinogenic. Further details on boron toxicity in humans and animals are described by CCME (1991), WHO (2004a) and US EPA (2008b).

The Australian drinking water guideline for boron is 4 mg/L. Canadian drinking water guidelines report a maximum limit of 5 mg/L (CCME 1991) and a tolerable daily intake (TDI) of 0.16 mg/kg body weight was derived by WHO (2004a).

4.6.10. Uranium

4.6.10.1. Environmental Hazards

Uranium occurs in natural waters in three oxidation states: $(IV) U_4^+$, $(V) UO_2^+$ and $(VI) UO_2^{2^+}$. In oxidised surface waters $UO_2^{2^+}$ (uranyl ion) is present and considered to be primarily responsible for causing toxicity. The uranyl ion forms stable and readily soluble complexes which are highly mobile. In contrast, in reducing waters U(IV) forms precipitates and remains immobile while U(V) forms soluble, but relatively unstable, complexes. The speciation of uranium is relatively complex in oxidised fresh surface waters (pH 5-9). Factors that affect the toxicity of uranium to aquatic biota include water hardness, pH, alkalinity, complexing agents (e.g. dissolved organic matter, carbonate) and sorption (to clay minerals, iron, aluminium (oxy)hydroxides, silica and micro-organisms) (ANZECC/ARMCANZ 2000).

The Australian water quality guideline for freshwaters is 0.5 μ g/L and is of low reliability (ANZECC/ARMCANZ, 2000). A recent uranium guideline for freshwaters was derived in Canada for short-term exposures (33 μ g/L) and long-term exposures (15 μ g/L) (CCME 2011).

CCME (2011) reported chronic toxicity to five fish species (EC/LC10 and MATC 350 to 14,300 μ g/L), an amphipod (EC10 of 12 μ g/L), three cladocerans (EC10 73-930 μ g/L), two aquatic plants (EC10 172 and 3,100 μ g/L) and a microalga (EC10 40 μ g/L). Acute toxicity included eight fish species (LC50 1,670-46,000 μ g/L) and three cladocerans (LC50 72-6,400 μ g/L).

In seawater, dissolved uranium predominantly exists as the uranyl-tricarbonate complex $(UO_2(CO_3)_3)^{4-})$ with smaller fractions of uranyl forming complexes with dissolved organic matter. No guideline values are reported for uranium in seawater due to a lack of toxicity data (ANZECC/ARMCANZ 2000; CCME 2011).

Uranium can bioaccumulate in aquatic organisms, although it does not biomagnify through the food chain (CCME 2011)

4.6.10.2. Human Health Hazards

The toxicity of uranium to human (and animal) health has been reviewed by WHO (2004c) the Swedish National Food Administration (Svensson et al. 2005), the United Kingdom Committee on Toxicity (COT 2006), and Health Canada (2001). Uranium is not regarded as an essential element (WHO 2004). The uranium drinking water guideline in Australia is 0.017 mg/L (NRMMC 2011) and WHO (2012) report a provisional guideline of 0.030 mg/L. The absorption of uranium in gastrointestinal tract is dependent on the solubility of the uranium compound ingested (typically 1-2%). Uranium rapidly appears in the bloodstream and uranyl compounds combine with proteins and nucleotides to form stable complexes. Clearance of uranium from blood is rapid but it accumulates in the kidneys and bone. The main toxic effects of short-term exposure to high concentrations of uranium is inflammation of the kidney. Little information on long-term effects to low concentrations is available. Epidemiological studies report possible kidney proximal tubule damage at drinking water concentrations of between 0.1 and 1 mg/L, but not at lower concentrations (NRMMC 2011). A tolerable daily intake (TDI) of 0.0006 mg/kg body weight has been derived by WHO (2004) and Health Canada (2001). No data is available on the chemically induced mutagenic effects of uranium. The Australian drinking water guideline is also considered to be protective of radiological effects.

4.6.11. Barium

4.6.11.1. Environmental Hazards

Barium compounds that do not dissolve well in water, such as barium sulfate and barium carbonate, can persist in the environment. Barium compounds that dissolve easily in water (such as barium chloride, barium nitrate, or barium hydroxide), usually do not last with dissolved barium quickly combining with sulfate or carbonate naturally found in water to become insoluble barium compounds (barium sulfate, barium carbonate). These insoluble barium compounds are most commonly found in soil, water and sediments (ATSDR 2007a).

Water quality guidelines for barium do not exist in Australian or other international jurisdictions (e.g. USA, Canada, UK). The US EPA (2006) summarised the acute toxicity of barium to aquatic organisms with EC50 values of 14.5 to 6,950 mg Ba/L (organisms included a cladoceran, tubificid worm, crayfish, amphipods and mosquitofish).

4.6.11.2. Human Health Hazards

The Australian drinking water guideline for barium is 2 mg/L (NHMRC 2011). The US EPA (2006) also report a guideline value of 2 mg/L and WHO (2004a) report a highly conservative guideline of 0.7 mg/L. Barium is not considered an essential element for humans and a number of reviews on the human and animal toxicity data for barium can be found in IPCS (2001a), OEHHA (2003), WHO (2004a), US EPA (2005) and ATSDR (2007a). In humans, cardiovascular effects (hypertension) have been observed after ingesting acutely high doses of barium compounds, and after inhalation of dusts of barium ores and barium carbonate. Some people who eat or drink somewhat smaller amounts of barium for a short period may experience vomiting, abdominal cramps, diarrhoea, difficulties in breathing, increased or decreased blood pressure, numbness around the face, and muscle weakness. One study showed that people who drank water containing as much as 10 mg/L of barium for 4 weeks did not have increased blood pressure or abnormal heart rhythms (ATSDR 2007a). The toxicity of barium salts is related largely to their solubility, which conditions their digestive absorption and bioavailability. Water and acid soluble salts are very toxic when ingested and absorbed barium mainly deposits in bone (about 90%). There is no evidence that barium is a carcinogen or mutagenic and insufficient evidence exists to suggest inhalation of barium salts are carcinogenic (ATSDR 2007a).

4.6.12. Arsenic

4.6.12.1. Environmental Hazards

Several forms of arsenic are present in the environment with the most common being As(III) or arsenite and As(V) or arsenate. As(V) is generally the most stable form in oxygenated environments (e.g. surface waters) while As(III) dominates under reducing conditions (e.g. groundwaters) (Appelo and Postma 2004). In general, As(III) is more toxic than As(V), except for plants. The Australian water quality guideline for freshwaters is 24 µg/L for As(III) and 13 µg/L for As(V). Water quality guidelines for As in marine waters are 2.3 µg/L for As(III) and 4.5 µg/L for As(V) but are of a low reliability. Toxicity of arsenic to aquatic biota is summarised by US EPA (1995), Vaughan (1996) and ANZECC/ARMCANZ (2000). Australian sediment quality guidelines also exist for Arsenic (total) of 20 (low) and 70 (high) mg/kg (dry weight).

Biotransformation of arsenic occurs in the environment via redox transformation, methylation and biosynthesis of organoarsenic compounds. Aquatic organisms bioconcentrate arsenic, primarily algae and lower invertebrates (WHO 2001). Bioconcentration factors (BCF) measured in freshwater invertebrates were generally up to 20 and were <5 for fish (detailed summary of studies provided in WHO 2001).

4.6.12.2. Human Health Hazards

Arsenic is one of WHOs 10 major public health concerns and classified as a carcinogen to humans. Long-term exposure to inorganic arsenic occurs mainly through drinking contaminated water, eating food prepared with contaminated water and eating food irrigated with arsenic-rich water, and can lead to chronic arsenic poisoning. Skin lesions and skin cancer are characteristic effects with bladder, kidney and lung also evident. Extensive reviews and summaries on human and animal toxicity are available (IPCS 2001, WHO 2003, IARC 2004, Health Canada 2006, ATSDR 2007b). Epidemiological studies have shown that elevated cancer risks and other adverse health effects are not demonstrated at arsenic concentrations of 10 μ g/L. Higher concentrations (50-100 μ g/L) have demonstrated a range of health effects including skin, lung and bladder cancer; skin pigmentation and keratosis; diseases of the lung, liver, vascular system; peripheral neuropath; and diabetes (NRMMC 2011). The Australian drinking water guideline for arsenic is 10 μ g/L, the same as that reported by the WHO (2004), European Union (1998), Health Canada (2008), US EPA (2008a) and New Zealand (MoH NZ 2008).

4.6.13. Summary of PNEC and drinking water guideline values

Based on the above toxicity data, PNEC data have been obtained for five out of twelve chemicals (Table 4-11). These PNEC values are for the protection of freshwater surface water biota, and not groundwater biota. Hence, they would be appropriate if the chemicals were to potentially reach surface water environments. Drinking water guideline values based on the Australian Drinking Water Guidelines (NHMRC and NRMMC 2011) have been obtained for four out of twelve chemicals (Table 4-11).

A PNEC values may be derived for limonene, HMX and bronopol. However, this requires a thorough literature search, followed by an assessment (and scoring) of each toxicity value following the approach described in Warne et al. (2015) and Batley et al. (2015). Such an assessment is beyond the scope of the current project.

CAS No.	CAS Chemical Name	PNEC (mg/L) ^a	Drinking water guideline value (mg/L) ^b
95-48-7	2-methylphenol (o-cresol)	NR	NR
91-20-3	naphthalene	0.016 ^c	NR
138-86-3	limonene	NR	NR
2691-41-0	HMX	NR	NR
111-76-2	2-butoxyethanol	0.165 ^d	NR
52-51-7	bronopol	NR	NR
26172-55-4	MCI	NR	NR
9003-05-8	acrylamide polymer	NR	NR
10043-35-3	boron (boric acid, H₃BO₃)	0.830 ^e	4
7440-61-1		0.0005 ^f	0.0017
	uranium	0.015 ^g	
7440-39-3	barium	NR	2
7440-38-2	arsenic	0.013 – As(V) ^h 0.024 – As(III) ^h	0.01

Table 4-11 Predicted no effect concentrations (PNEC) for the protection of aquatic freshwater biota and drinking water guideline concentrations for Australia.

^a Australian and New Zealand water quality guideline values (PC95 values; ANZECC/ARMCANZ 2000) unless stated otherwise; ^b Australian Drinking Water Guideline (NHMRC and NRMMC 2011); ^c Moderate reliability (ANZECC/ARMCANZ 2000); ^d Based on the toxicity of the freshwater fish golden ide (*Leuciscus idus melanotus*) 48-h LC50 (165 mg/L) divided by an assessment factor of 1000 for protection of freshwater and estuarine environment (WHO 1998); ^e Revised water quality guideline submitted to the Department of Agriculture and Water Resources, September 2016. Very high reliability; ^f Low reliability guideline value (ANZECC/ARMCANZ 2000); ^g Long-term water quality guideline for freshwaters reported by the Canadian Council of Ministers of the Environment (CCME 2011) may also be used as a PNEC value in addition to ANZECC/ARMCANZ (2000) value of 0.0005 mg/L; ^h High reliability (ANZECC/ARMCANZ 2000); NR = Not reported; [#] = PNEC values were derived based on the metal dissolved in aqueous media, hence, various CAS numbers would be applicable and dependent on the metal salt being investigated.

5. Composite research product

5.1. Methodology

The composite research product provides a two-level screening (Figure 5-1): at Level-1, chemicals will be screened that have previously been rigorously assessed and found to be of low concern to the environment or human health (that is, "chemicals of low concern"). At the Level-2 analysis, chemicals not screened out at Level 1 are now assessed to determine:

- existence of connecting pathways between a hydraulic fracturing-related chemical source and receptors, and if such pathway exists the likely travel time from source to receptor,
- the potential for chemical/biological, geological (owing to chemical sorption onto organic and/or mineral phases) and flow-related (dilution/dispersion) attenuation of coal seam gas chemicals (hydraulic fracturing and geogenic chemicals) in deeper groundwater systems,
- a dilution attenuation factor (DAF) that takes account of the previous pathway and attenuation information to allow ranking of the relative hazard and to determine setback distances that ensure protection of human health and the environment.

In deriving setback distances one may reasonably assume the combined attenuation processes would result in concentrations of hydraulic fracturing chemicals that would not cause a negative impact on human health and the environment. Also, setback distances are a legislative method to mitigate potential risks (DEHP 2013; NSW Chief Scientist and Engineer 2014d).



Figure 5-1 Two-level hazard screening approach for drilling and hydraulic fracturing chemicals.

Details from the Level-1 screening are available from Section 2.2 and will not be repeated here. The Level-2 analyses combine (Figure 5-2): i) the spatial analyses of contaminant source-receptor distance-frequency relationships (Section 3.2 and 3.3), ii) chemical, biological and geological attenuation information for characteristic chemicals (Section 4), and iii) the

conceptual models, application protocols and calculation tools required to estimate the likelihood that the chemical could reach and impact receptors (Section 2.6.4 and 2.6.5). These components are integrated in the hazard screening framework to generate the DAF for each chemical.

The final hazard screening tool has both site-dependent and site-independent elements. Reseach Product 1 is the hazard screening tool that can be used to identify i) chemicals of low concern to human health and the environment that do not need further assessments, and ii) chemicals that cannot be classified as 'of low concern' and therefore require further assessments. The Level-1 screening (Product 1) is site-independent, as it does not include site-specific exposure assessments.

Research Product 2 provides an assessment of chemical pathways between sources of CSG chemicals in deeper groundwater and groundwater related receptors. The pathways are calculated on the basis of particle tracking analysis and deliver source-receptor transport distance and corresponding travel time. The chemical transport pathway analysis of Product 2 is site-dependent (Figure 5-2); however, by using two different case study areas a broad set of flow conditions will be generated giving the final analysis a high level of generality.

Research Product 3 involves a spatial analysis to establish proximities (horizontal distances) between CSG well locations and a series of ecologic, economic and cultural receptors. Research Product 3 is site-dependent (Figure 5-2), but will again cover a wider range of proximity data which allows making some general statements about likelihood of exposure.

Research product 4 includes a compilation of attenuation parameters (K_{OC} and half-life [$t_{1/2}$] for organics and K_d for inorganics) for relevant chemicals, coal target formations and aquifers considered in this study. Research Product 4 is in part site-independent (K_{OC} , K_{OW} , possibly $t_{1/2}$), and in part site-dependent (K_d , using site-specific sorption data based on site-specific organic carbon information; although the sorption data will be very poor and at best some broad classes covering most of the relevant geology will be defined).

Research product 5 provides the dilution attenuation factors – DAF – developed as part of this research. This final product is site-specific, although the approach taken will give it some degree of generality.

When selecting the case study areas, care has been taken to have a sufficiently broad coverage of hydrogeological conditions and features (faults, springs, ...) that will give the analysis a sufficient level of generality, rather than being too site-specific. Nevertheless, this analysis cannot describe all possible conditions one may encounter in all Australian CSG basins. The nuts and bolts of the hazard screening framework will be illustrated on the basis of the case studies, without claiming to provide a nation-wide coverage. The analysis undertaken with the screening framework should provide insights to address the questions regarding potential deep groundwater contamination. On the basis of these insights, one can then discuss the need for similar analyses in other basins, and what questions are relevant in other basins (e.g. if faults turn out to be the only conceivable pathway, then the focus turns on basins with faults near extraction areas).



Figure 5-2 Possible workflow of the hazard screening framework.

5.2. Application to the Gunnedah Basin

5.2.1. Organic substances

5.2.1.1. Attenuation due to chemical/biological degradation

A summary of half-life values for aerobic and anaerobic degradation and hydrolysis is provided in Table 5-1. When available, minimum and maximum values obtained from the literature review are shown. No data was found for Acrylamide polymer; for this substance it is assumed it will not degrade. Half-life values were used to calculate the final concentration at a receptor for a given travel time using equation (1), where travel time was calculated by means of particle tracking (Section 2.6.4.4). A hypothetical concentration of 1 (without specific units) was used in the calculations of the dilution factor. Section 5.6 provides examples of how dilution factors thus derived can be used in the context of protection of ecosystems and human health.

Calculations are done first using the default half-life values without consideration of specific hydrostratigraphic units. This was done to explore attenuation behaviour across the full range of values. In Section 5.2.1.2, the dilution attenuation will be calculated for each hydrostratigraphic unit by accounting for layer-specific half-life values.

Travel times used in the calculations are the most conservative values encountered in the particle tracking analysis, and are based on the Pilliga Sandstone, Gunnedah Basin. Calculations of chemical/biological degradation used the minimum (10 y), mean (34 y), and maximum (92 y) travel time in the first travel time class (from 0 to 100 years) as given in Section 2.6.4.4, Table 2-24. Travel times for all other relevant aquifers including Maules Creek (Gunnedah) and all Surat aquifers (Table 2-26) are much larger, hence would result in an even larger degradation that what is calculated based on the Pilliga Sandstone values. Dilution attenuation factors (DAF) are calculated as follows (where half-life data was available):

$$DAF = \frac{1}{C_F} \tag{17}$$

where C_F is chemical concentration at receptor accounting for degradation, sorption and dilution.

Table 5-1 Half-life data used in attenuation calculations. Values represent observed range based on in situ and field studies. MCI = Methyl-chloro
isothiazolinone. NBD = not biodegradable . Values rounded to three significant figures. N.d. = no data; n.a. = not applicable.

	Half-life (days)								
	Ana	erobic	Aer	obic	Hydrolysis				
Chemical substance	Min	Max	Min	Max	Min	Max			
2-methylphenol	20	1,390	1.6	5.1	n.a.	n.a.			
Naphthalene	96	NBD	2.1	88	n.a.	n.a.			
Limonene	n.a.	n.a.	2.3	18	n.a.	n.a.			
НМХ	2.3	2.3	15	15	21.1	31.2			
2-butoxyethanol	28	112	7	56	n.a.	n.a.			
Bronopol	n.d.	n.d.	n.d.	n.d.	0.094	60			
MCI	5	5	0.21	0.21	22	22			
Acrylamide- polymer	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.			

5.2.1.1.1. 2-methylphenol

Decrease in 2-methylphenol concentration as function of travel time is displayed in Figure 5-3. At its minimum and maximum aerobic half-life and minimum anaerobic half-life, 2-methylphenol degrades quickly and within less than 200 days has almost completely disappeared from solution. Only for the maximum anaerobic half-life value does 2-methylphenol degrade much slower, i.e. after 400 days the final concentration at a receptor would be at 80% of its original value.



Figure 5-3 Relative concentration for 2-methylphenol as a result of chemical/biological degradation. Minimum and maximum half-lives are used for aerobic and anaerobic degradation.

The same calculations are shown for a much longer time-axis, i.e. until 4,000 days (Figure 5-4). The relatively slow degradation of 2-methylphenol for a maximum anaerobic half-life value is evident; after 3,660 days (10 years, i.e. the minimum travel time in Pilliga Sandstone), the final concentration at a receptor (C_F) has decreased to a value of 0.16, which is equivalent to a DAF of 1/0.16 = 6.2. The dilution factors for the other half-life values are extremely large (i.e. > 1E+10).



Figure 5-4 Relative concentration for 2-methylphenol as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_r) derived for minimum solute travel time T_{min} of 3,660 days. Minimum and maximum half-lives used for aerobic and anaerobic degradation.

A final analysis of 2-methylphenol degradation is shown in Figure 5-5. Here the final concentration and corresponding DAF values are obtained for three travel times, i.e. minimum (10 years), mean (12,300 days or 34 years) and maximum (33,500 days or 92 years) (for the travel time class #1, Table 2-24). For minimum, mean, and maximum travel time the DAF values are 6.2, 475, and 1.5E+7. To put these numbers in perspective, calculated DAF values from US EPA (1994c) are provided as comparison; for a 93 m² source area the DAF value in groundwater at 0.3 m distance from the edge of the source was 1E6.



Figure 5-5 Relative concentration for 2-methylphenol as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days), mean (12,300 days) and maximum (33,500 days) solute travel time for travel time class # 1 (Table 2-24). Minimum and maximum half-lives used for anaerobic degradation.

5.2.1.1.2. Naphthalene

Under aerobic degradation with minimum and maximum half-lives and for anaerobic degradation with minimum half-life, naphthalene displays a relatively fast degradation (Figure 5-6). After 400 days following release, the concentrations have decreased to less than 10% of the original source value.

For travel times up to 4,000 days, final concentrations decrease to negligible fractions of the source concentration, with DAF values of 3E+11 for minimum half-life (after 3,660 days of travel) and 6E+13 for aerobic degradation at maximum half-life (Figure 5-7).

For very long travel times up to 40,000 days, naphthalene will have completely degraded for all parameter combinations except one (Figure 5-8): under anaerobic conditions the maximum half-life is virtually infinity as naphthalene is very unlikely to degrade under those conditions.



Figure 5-6 Relative concentration for naphthalene as a result of chemical/biological degradation. Minimum and maximum half-lives used for aerobic and anaerobic degradation.



Figure 5-7 Relative concentration for naphthalene as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days) solute travel time for travel time class # 1 (Table 2-24). Minimum and maximum half-lives used for aerobic and anaerobic degradation.



Figure 5-8 Relative concentration for naphthalene as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days), mean (12,300 days) and maximum (33,500 days) solute travel time for travel time class # 1 (Table 2-24). DAF and C_F values for mean and maximum travel time are not shown ($C_F = 0$ and DAF = infinitely large). Minimum half-life used for anaerobic degradation.

5.2.1.1.3. Limonene

In case of aerobic degradation limonene degrades quickly for minimum and maximum half-lives (Figure 5-9). As a result of the fast degradation, the DAF value after 3,660 days of travel is extremely large (i.e. infinity) (Figure 5-10).



Figure 5-9 Relative concentration for limonene as a result of chemical/biological degradation. Minimum and maximum half-lives used for aerobic degradation.



Figure 5-10 Relative concentration for limonene as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days) solute travel time for travel time class # 1 (Table 2-24). Minimum and maximum half-lives used for aerobic degradation.

5.2.1.1.4. HMX

In the event that hydrolysis takes place, HMX will decrease rapidly to negligible concentrations (Figure 5-11). After 3,660 days of travel the concentrations at the receptor are effectively zero and the DAF value is infinity (Figure 5-12).



Figure 5-11 Relative concentration for HMX as a result of chemical/biological degradation. Minimum and maximum half-lives used for anaerobic and aerobic degradation and hydrolysis.



Figure 5-12 Relative concentration for HMX as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days) solute travel time for travel time class # 1 (Table 2-24). Minimum and maximum half-lives used for anaerobic and aerobic degradation and hydrolysis.

5.2.1.1.5. 2-butoxyethanol

When aerobic degradation of 2-butoxyethanol occurs concentrations become negligible after 100 days of travel (Figure 5-13). Under aerobic (minimum and maximum half-lives) and anaerobic (minimum half-life) conditions a DAF value of infinity (i.e. > 1E10) is obtained 3,660 days after release of the source (Figure 5-14).



Figure 5-13 Relative concentration for 2-butoxyethanol as a result of biological degradation. Minimum and maximum half-lives used for anaerobic and aerobic degradation.



Figure 5-14 Relative concentration for HMX as a result of biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_r) derived for minimum (3,660 days) solute travel time for travel time class # 1 (Table 2-24). Minimum and maximum half-lives used for anaerobic and aerobic degradation.

5.2.1.1.6. Bronopol

Bronopol degradation by means of hydrolysis is relatively fast, even for the largest half-life value (Figure 5-15). Complete degradation has occurred after 3,660 days since release from the source, yielding DAF values for all half-lives of infinity (Figure 5-16).



Figure 5-15 Relative concentration for bronopol as a result of chemical degradation. Minimum and maximum half-lives used for hydrolysis.



Figure 5-16 Relative concentration for bronopol as a result of chemical degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days) solute travel time for travel time class # 1 (Table 2-24). Minimum and maximum half-lives used for hydrolysis.

5.2.1.1.7. Methyl-chloro-isothiazolinone

Three degradation mechanism were identified for methyl-chloro-isothiazolinone, i.e. hydrolysis and aerobic/anaerobic degradation. Based on the available half-life values, degradation is complete within 200 days following release (Figure 5-17). All degradation mechanisms result in a DAF value of infinity after 3,660 days (Figure 5-18).



Figure 5-17 Relative concentration for MCI as a result of chemical/biological degradation. Maximum half-lives used for anaerobic and aerobic degradation and hydrolysis.



Figure 5-18 Relative concentration for MCI as a result of chemical/biological degradation. Dilution attenuation factor (DAF) and final concentration at receptor (C_F) derived for minimum (3,660 days) solute travel time for travel time class # 1 (Table 2-24). Maximum half-lives used for anaerobic and aerobic degradation and hydrolysis.

5.2.1.1.8. Summary of attenuation calculations

The first series of attenuation calculations discussed in the previous sections accounted for aerobic and anaerobic degradation and hydrolysis. The final concentration remaining at a receptor when three different travel times were accounted for (minimum, mean, and maximum), was calculated and summarised in Table 5-2 to Table 5-4. Minimum,

mean and maximum travel time were taken from the first travel time class (between 0 and 100 years), see Table 2-24 for the Gunnedah Basin.

From the three degradation processes, anaerobic biodegradation and hydrolysis are the most relevant for the deeper groundwater investigations. Aerobic biodegradation is relevant in shallow, alluvial groundwater. Therefore, attenuation potential is primarily based on consideration of anaerobic biodegradation and hydrolysis. Whenever half-life values for these two processes were available, they take preference over the aerobic biodegradation ones. When both anaerobic biodegradation and hydrolysis occurs, the highest relative concentration at receptor is chosen: this is a conservative approach and accounts for uncertainties about the degree of degradation due to lack of data on site-specific attenuation potential. If neither anaerobic biodegradation nor hydrolysis occurs, then aerobic degradation could be invoked - provided its half-life values are available - where the pathway traverses shallow oxygenated groundwater.

Based on the calculated relative concentrations at receptor after three different travel times Table 5-2 to Table 5-4), the eight chemical substances considered belong to one of four groups:

- Group 1 chemicals (HMX and MCI) have a maximum of three modes of degradation (anaerobic biodegradation and hydrolysis relevant for deeper groundwater and aerobic degradation relevant for shallow oxygenated groundwater) and degrade completely within 10 years of travel time.
- Group 2 chemicals (2-methylphenol, naphthalene, 2-butoxyethanol, bronopol) have at least one mode of degradation relevant for deeper groundwater (either anaerobic biodegradation or hydrolysis) and degrade partially within 10 years or completely within 34 or 90 years.
- Group 3 chemicals (limonene) only have the degradation mode for shallow groundwater and degrade completely within 10 years.
- Group 4 chemicals (acrylamide polyer) do not have any degradation mode and therefore remain at their initial concentration of one.

Relative concentration (-) at receptor: minimum travel time							
	Anae	robic	Aer	obic	Hydrolysis		
Chemical substance	Min	Max	Min	Max	Min	Max	
2-methylphenol	0	0.16	0	0	1	1	
Naphthalene	3.3E-12	1	0	3.0E-13	1	1	
Limonene	1	1	0	0	1	1	
НМХ	0	0	0	0	0	0	
2-butoxyethanol	0	0	0	2E-20	1	1	
Bronopol	1	1	1	1	0	4.3E-19	
MCI	0	0	0	0	0	0	
Acrylamide polymer	1	1	1	1	1	1	

Table 5-2 Calculated relative concentration at receptor for minimum travel time of 10 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Initial source concentration is 1 (no units specified). Numbers in italics assume absence of chemical/biological degradation.

Dilution attenuation factors (DAF) are calculated on the basis of the remaining concentration at the receptor, i.e. DAF = $1/C_{\rm F}$. DAF values are generally very large for chemicals that have at least one mode of degradation. Note that DAF values > 1E+10 were cut off at 1E+10. In other words, most dilution factors are practically infinite but for reasons of presentation have been put at 1E+10. Group 2 chemical 2-methylphenol has a much smaller DAF value (from 6.2 after 10 years (Table 5-5), 475 after 34 years (Table 5-6) and 1.85E7 after 92 years (Table 5-7)) based on its maximum half-life. Naphthalene has the smallest possible DAF value (one) based on its maximum half-life, irrespective of travel time (Table 5-5, Table 5-6 and Table 5-7).

Table 5-3 Calculated relative concentration at receptor for mean travel time of 34 years (travel time class # 2 Table 2-24). MCI = Methyl-chloro-isothiazolinone. Initial source concentration is 1 (no units specified). Numbers in italics assume absence of chemical/biological degradation.

		Relative cond	centration (-)	entration (-) at receptor : mean travel time			
	Ana	erobic	Aei	Aerobic		Hydrolysis	
Chemical substance	Min	Max	Min	Max	Min	Max	
2-methylphenol	0	0.0021	0	0	1	1	
Naphthalene	0	1	0	0	1	1	
Limonene	1	1	0	0	1	1	
НМХ	0	0	0	0	0	0	
2-butoxyethanol	0	0	0	0	1	1	
Bronopol	1	1	1	1	0	0	
MCI	0	0	0	0	0	0	
Acrylamide polymer	1	1	1	1	1	1	

Table 5-4 Calculated relative concentration at receptor for maximum travel time of 92 years (travel time class # 3 Table 2-24). MCI = Methyl-chloroisothiazolinone. Initial source concentration is 1 (no units specified). Numbers in italics assume absence of chemical/biological degradation.

Relative concentration (-) at receptor: maximum travel time							
	Ana	aerobic	Aer	Aerobic		Hydrolysis	
Chemical substance	Min	Max	Min	Max	Min	Max	
2-methylphenol	0	5.4E-8	0	0	1	1	
Naphthalene	0	1	0	0	1	1	
Limonene	1	1	0	0	1	1	
НМХ	0	0	1	1	0	0	
2-butoxyethanol	0	0	0	0	1	1	
Bronopol	1	1	1	1	0	0	
MCI	0	0	0	0	0	0	
Acrylamide polymer	1	1	1	1	1	1	

Table 5-5 Calculated dilution attenuation factor (DAF) at receptor for minimum travel time of 10 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Numbers in italics assume absence of chemical/biological degradation.

Dilution attenuation factor (-) at receptor: minimum travel time							
	Anae	erobic	Aei	Aerobic		Hydrolysis	
Chemical substance	Min	Max	Min	Max	Min	Max	
2-methylphenol	1E+10	6.24E+00	1E+10	1E+10	1	1	
Naphthalene	1E+10	1E+00	1E+10	1E+10	1	1	
Limonene	1	1	1E+10	1E+10	1	1	
HMX	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	
2-butoxyethanol	1E+10	6.94E+09	1E+10	1E+10	1	1	
Bronopol	1	1	1	1	1E+10	1E+10	
MCI	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	
Acrylamide polymer	1	1	1	1	1	1	

Table 5-6 Calculated dilution attenuation factor (DAF) at receptor for mean travel time of 34 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Numbers in italics assume absence of chemical/biological degradation.

	ean travel time						
	Ana	erobic	Aer	Aerobic		Hydrolysis	
Chemical substance	Min	Max	Min	Max	Min	Max	
2-methylphenol	1E+10	4.75E+02	1E+10	1E+10	1	1	
Naphthalene	1E+10	1E+00	1E+10	1E+10	1	1	
Limonene	1	1	1E+10	1E+10	1	1	
НМХ	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	
2-butoxyethanol	1E+10	1E+10	1E+10	1E+10	1	1	
Bronopol	1	1	1	1	1E+10	1E+10	
MCI	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	
Acrylamide polymer	1	1	1	1	1	1	

Table 5-7 Calculated dilution attenuation factor (DAF) at receptor for maximum travel time of 92 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Numbers in italics assume absence of chemical/biological degradation.

	Dilution factor at receptor (-): maximum travel time							
	Ana	erobic	Aero	Aerobic		olysis		
Chemical substance	Min	Max	Min	Max	Min	Max		
2-methylphenol	1E+10	1.85E+07	1E+10	1E+10	1	1		
Naphthalene	1E+10	1E+00	1E+10	1E+10	1	1		
Limonene	1	1	1E+10	1E+10	1	1		
НМХ	1E+10	1E+00	1E+10	1E+10	1E+10	1E+10		
2-butoxyethanol	1E+10	1E+00	1E+10	1E+10	1	1		
Bronopol	1	1	1	1	1E+10	1E+10		
MCI	1E+10	1E+00	1E+10	1E+10	1E+10	1E+10		
Acrylamide polymer	1	1	1	1	1	1		

5.2.1.2. Attenuation due to chemical/biological degradation and sorption

In a second series of calculations both chemical/biological degradation and sorption was considered. Sorption of organic compounds onto organic carbon was accounted for by implementing Equation (3). The compound-specific distribution coefficients K_d used for the Gunnedah and Surat Basin were derived based on compound-specific baseline K_{OC} values and the rescaled fraction of organic carbon (f_{OC_r}). The f_{OC_r} values representative of Gunnedah Basin and Surat Basin hydrostratigraphic units are summarised in Table 5-8. Three broad groups of f_{OC_r} values can be distinguished:

- Negligible organic carbon (f_{OC_r} = 0): the sandstone aquifers of the Pilliga Sandstone and the Upper and Lower Maules Creek (Gunnedah) and several Surat aquifers.
- Low organic carbon (f_{OC_r} = 0.0008 0.001): the alluvial aquifers and the shales and siltstones of the Blythesdale Group (Gunnedah Basin) and the Gubberamunda Sandstone (Surat Basin).
- High organic carbon (f_{oc_r} = 0.0126 0.275): coal seam aquifers (Hoskisson and Maulus Creek-Bohena and Walloon Coal Measures).

For the first group ($f_{OC_r} = 0$), no additional dilution due to adsorption processes is considered. The concentration at receptor calculated in the previous section remains unchanged.

For the second group (a single value of f_{OC_r} = 0.001 is considered) the K_{OC} values based on the literature survey (Appendix 5) are converted into K_d values (Table 5-9). At present there was insufficient data to assume a major difference in sorption properties for the key aquifers in both basins. As a result, calculations are carried out once and are not reported separately

for the two basins. On the basis of the K_d values, the retardation factor R_f was derived using Equation (1), assuming a dry bulk density of 1.6 g/cm³ and a total porosity of 0.1 cm³/cm³; calculated values for R_f are summarised in Table 5-10.

Gunnedah Basin	foc_r (g∕g)	Surat Basin	f _{oc_r} (g/g)
Namoi alluvium	0.001	Dawson River alluvium	0.001
Pilliga Sandstone	0	Bungil Formation-Mooga Sandstone-Orallo Formation (BMO Group)	0
Blythesdale Group	0.0008	Gubberamunda Sandstone	0.0008
Hoskisson seam	0.275	Westbourne Formation	0
Maules Creek Formation (upper)	0	Springbok Sandstone	0
Maules Creek Formation (Bohena coal measures)	0.275	Walloon Coal Measures	0.0126
Maules Creek Formation (lower)	0	Hutton Sandstone	0

Table 5-8 Summary of fraction of organic carbon (f_{OC_r}) for Gunnedah and Surat Basin aquifers.

Table 5-9 Sorption data (K_{oc} and distribution coefficient $K_d = f_{oc_r} \times K_{oc}$ with $f_{oc_r} = 0.001$) used for attenuation calculations. MCl = Methyl-chloro-isothiazolinone. Values rounded to three significant figures.

	Sorption data, K _{oc} (L/kg)		Sorption data, <i>K</i> _d (L/kg)				
	Base	line	Gunneda	Gunnedah		Surat	
Chemical substance	Min	Max	Min	Max	Min	Max	
2-methylphenol	22	251	0.022	0.3	0.022	0.3	
Naphthalene	17	26,900	0.017	26.9	0.017	26.92	
Limonene	1,000	58,900	1.000	58.9	1.000	58.9	
НМХ	32	1,260	0.032	1.26	0.032	1.26	
2-butoxyethanol	2.9	8	0.003	0.008	0.003	0.008	
Bronopol	0.9	1,410	0.001	1.41	0.001	1.41	
MCI	30	143	0.030	0.14	0.030	0.14	
Acrylamide polymer	25	398	0.025	0.40	0.025	0.40	

In the third group of aquifers organic carbon is high due to the presence of coal seam layers, with a distinct difference between the Gunnedah ($f_{OC_r} = 0.275$) and Surat Basin ($f_{OC_r} = 0.0126$). The calculated K_d values and retardation factors R_f are listed in Table 5-11 and Table 5-12, respectively. Large retardation factors are observed for most compounds. The chemical concentrations at receptor were not calculated because nearly all compounds that could be affected by the combined effects of degradation and sorption displayed already zero concentrations even at a much lower f_{OC_r} value of 0.001 (Table 5-13 to Table 5-15). The exception is 2-methylphenol at a minimum anaerobic degradation: its concentration decreased from 0.08 (retardation $R_f = 1.4$) to zero when higher sorption was accounted for (retardation $R_f = 52$ or higher). The effect of increasing retardation on the calculated concentrations at receptors is displayed in Figure 5-19. From retardation factors of around $R_f = 50$ onwards concentrations drop rapidly to zero within 200 days or less.

	Retardation factor, R_f (-)					
	Gunr	nedah	Su	irat		
Chemical substance	Min	Max	Min	Max		
2-methylphenol	1.4	5	1.4	5		
Naphthalene	1.3	432	1.3	432		
Limonene	17	943	17	943		
НМХ	1.5	21.1	1.5	21.1		
2-butoxyethanol	1.0	1.1	1.0	1.1		
Bronopol	1.0	23.6	1.0	23.6		
MCI	1.5	3.3	1.5	3.3		
Acrylamide polymer	1.4	7.4	1.4	7.4		

Table 5-11 Sorption data (K_{oc} and distribution coefficient $K_d = f_{oC_r} \times K_{oc}$ with $f_{oC_r} = 0.275$ for Gunnedah and 0.0126 for Surat) used for attenuation calculations. MCI = Methyl-chloro-isothiazolinone. Values rounded to three significant figures.

	Sorption data, K _{oc} (L/kg)		Sorption data, K _d (L/kg)			
	Base	line	Gunne	Gunnedah		at
Chemical substance	Min	Max	Min	Max	Min	Max
2-methylphenol	22	251	6.0	69	0.28	3.2
Naphthalene	17	26,900	4.7	7,400	0.21	339
Limonene	1,000	58,900	275	16,200	12.60	742
НМХ	32	1,260	8.7	346	0.40	15.9
2-butoxyethanol	2.9	8	0.8	2.2	0.04	0.1
Bronopol	0.9	1,410	0.3	388	0.01	17.8
MCI	30	143	8.3	39	0.38	1.8
Acrylamide polymer	25	398	6.9	109	0.32	5.0

Table 5-12 Sorption data (R_f) (rounded to three significant figures) used for attenuation calculations (f_{oc_r} = 0.275 for Gunnedah and 0.0126 for Surat). MCI = Methyl-chloro-isothiazolinone. Values rounded to three significant figures.

	Retardation factor, $R_f(-)$			
	Gunnedah		Surat	
Chemical substance	Min	max	min	max
2-methylphenol	97	1,110	5.4	52
Naphthalene	76	118,000	4.4	5,430
Limonene	4,400	259,000	203	11,900
НМХ	140	5,540	7.4	255
2-butoxyethanol	14	36	1.6	2.6
Bronopol	5.1	6,220	1.2	286
MCI	134	632	7.1	30
Acrylamide polymer	112	1,750	6.1	81

When the effect of both sorption and degradation is accounted for the second group (a single value of $f_{OC_r} = 0.001$ is considered), concentrations at the receptor are different only for 2-methylphenol, naphthalene and bronopol. For 2-methylphenol, concentration decreases from 0.16 (without sorption, Table 5-2) to 10^{-4} (at minimum travel time and maximum R_f) and from 0.0021 (without sorption, Table 5-2) to zero for mean travel times and maximum retardation R_f (Table 5-14). Naphthalene decreases from 3.3×10^{-12} (without sorption, minimum travel time and maximum anaerobic biodegradation, Table 5-2) to zero when sorption is accounted for. Bronopol concentration decreases from 4.3×10^{-19}
(without sorption, minimum travel time and maximum hydrolysis, Table 5-2) to zero when sorption is included. For the maximum travel time of 92 years there is no difference between concentrations calculated with or without sorption (Table 5-15).

Table 5-13 Calculated relative concentration at receptor for minimum travel time of 10 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Initial source concentration is 1 (no units specified). (f_{oC_r} = 0.001). Underlined numbers have their concentrations decreased compared to calculations without sorption. When two numbers are shown results represent minimum/maximum R_t values. Attenuation due to degradation and sorption.

	um travel time					
	Anae	erobic	Aero	obic	Hydrolysis	
Chemical substance	Min	max	min	max	min	max
2-methylphenol	<u>0</u>	<u>0.08/1E-4</u>	0	0	1	1
Naphthalene	<u>0</u>	1.00	0	<u>0</u>	1	1
Limonene	1 1		0	0	1	1
HMX	0	0	0	0	0	0
2-butoxyethanol	0	0	0	<u>0</u>	1	1
Bronopol	1	1	1	1	0	<u>0</u>
MCI	0	0	0	0	0	0
Acrylamide polymer	1	1	1	1	1	1

Table 5-14 Calculated relative concentration at receptor for mean travel time of 34 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Initial source concentration is 1 (no units specified). ($f_{OC_r} = 0.001$). Underlined numbers have their concentrations decreased compared to calculations without sorption. When two numbers are shown results represent minimum/maximum R_t values. Attenuation due to degradation and sorption.

		Relative cond	icentration (-) at receptor: mean travel time						
	Anaerobic		Aei	robic	Hydrolysis				
Chemical substance	Min Max		Min	Max	Min	Max			
2-methylphenol	0	<u>2.4E-4/0</u>	0	0	1	1			
Naphthalene	0	1.00	0	0	1	1			
Limonene	1 1		0	0	1	1			
НМХ	0	0	0	0	0	0			
2-butoxyethanol	0	0	0	0	1	1			
Bronopol	1	1	1	1	0	0			
MCI	0 0		0	0	0	0			
Acrylamide polymer	1	1	1	1	1	1			

Table 5-15 Calculated relative concentration at receptor for maximum travel time of 92 years (travel time class # 1 Table 2-24). MCI = Methyl-chloroisothiazolinone. Underlined numbers have their concentrations decreased compared to calculations without sorption. Initial source concentration is 1 (no units specified). ($f_{OC_r} = 0.001$). Attenuation due to degradation and sorption.

Relative concentration (-) at receptor: maximum travel time										
	Anaerobic		Aer	obic	Hydrolysis					
Chemical substance	Min Max		Min	Max	Min	Max				
2-methylphenol	0	<u>0</u>	0	0	1	1				
Naphthalene	0	1	0	0	1	1				
Limonene	1	1	0	0	1	1				
НМХ	0	0	0	0	0	0				
2-butoxyethanol	0	0	0	0	1	1				
Bronopol	1	1	1	1	0	0				
MCI	0	0	0	0	0	0				
Acrylamide polymer	1	1	1	1	1	1				



Figure 5-19 Comparison between relative concentration at receptor considering anaerobic biodegradation without sorption (R=1) and with sorption (various R_{t} values > 1). The fraction of organic carbon ($f_{oc_{x}}$) is indicated. Calculations based on minimum anaerobic biodegradation rate for 2-methylphenol.

5.2.1.3. Attenuation due to dilution and dispersion

So far, only the effects of chemical/biological degradation and sorption on chemical concentrations have been accounted for. The third attenuation process that will be included is the attenuation due to dilution and dispersion in groundwater. For this purpose, the three-dimensional advection-dispersion solute transport model based on the analytical solutions of Leij and Bradford (1994) is implemented. Several analytical solutions were reviewed (see Appendix 6); the solutions of Leij and Bradford (1994) were appropriate for three-dimensional advective-dispersive transport. Among the several solutions provided by Leij and Bradford (1994), the so-called initial value problem boundary condition (IVP) with a parallelepipedal source of finite duration in a rectangular coordinate system is most appropriate to represent an initial solute plume soon after it is injected into an aquifer (e.g. the fraction of the hydraulic fracturing fluid that is not returned to the surface following injection).

The parameters for the solute transport model are as follows: groundwater velocity was based on particle tracking calculations previously discussed for the Pilliga Sandstone (see section 2.6.4.4). The minimum arrival time (10 years) for the minimal transport distance (0.5 km) resulted in a conservative estimate of the particle velocity v = 0.14 m/day. The effect of slower velocities will also be discussed. Further transport parameters are longitudinal dispersion, D_L , assumed to be 1 m²/day, and the horizontal (D_{TH}) and vertical (D_{TV}) transverse dispersion assumed to be equal to 0.1 m²/day. The corresponding longitudinal dispersivity or dispersion length parameter λ_L is 7.14 m (such that $D_{L=}\lambda_L \times v$, *i.e.* 1 = 7.14×0.14); this is slightly smaller than one tenth of a 100 m travel distance (the rule of thumb for selecting dispersivity values in groundwater is about one tenth of the chemical's travel distance – Fetter 1993). Although travel distances of more than one km are used in the calculations, keeping the dispersivity at this small value is conservative (the smaller the dispersivity, the smaller the 'flattening' of the chemical breakthrough curve and the higher the maximum concentration at a receptor). Horizontal transverse dispersivity (λ_{TH} , with $D_{TH} = \lambda_{TH} \times v$) and vertical transverse dispersivity (λ_{TV} , with $D_{TV} = \lambda_{TV} \times v$) can range from about one-sixth to about one-twentieth of the longitudinal dispersivity (Fetter 1993); here we assumed $\lambda_{TH} = \lambda_{TY} = \lambda_{T}/10 = 0.714$ m.

The dimensions of the solute source considered in the advective-dispersive transport depends on a number of factors: the thickness of the coal seam targeted for fracturing, the number of hydraulic fracturing operations per well, and the volume

of injected hydraulic fracturing fluid. A final parameter that needs consideration is the density of wells; for wells that have a close spacing, the individual fracturing fluid plumes may amalgamate into a single plume.

In the Walloon Coal Measures there are up to 45 individual coal seams that may be hydraulically fractured. Their total thickness makes up less than 10% of the 300 m average total thickness of the Walloon Coal Measures (OGIA 2016). Only the most economical seams are fractured. The thickness of the seams varies from 0.8 to 6.3 m (Santos 2015). The fractures typically propagate up to a maximum distance of 100 m from the well (Santos 2015). The number of hydraulic fracturing operations per well, where required, were reported to vary between 1 and 9 (NICNAS 2017c). In Santos GLNGs' gas fields in the Surat Basin there are between 3 and 12 such coal seams that receive fracturing (Santos 2015). A range of injection volumes will be considered in the assessment to accommodate such range of conditions that may occur across different injection sites.

The cumulative frequency distribution of injected hydraulic fracturing volumes during 2014 across 7 production sites in QLD is shown in Figure 5-20 (each data point represents a separate fracture event; data provided by APPEA (2015)). The minimum, mean and maximum injected hydraulic fracturing volumes are 0.0083 ML (18% probability of non-exceedance), 0.914 ML (66% probability of non-exceedance), and 2 ML (99% probability of non-exceedance), respectively. Additional information on the volumes of formulations and individual chemicals injected into wells after final dilution for pre-treatment or hydraulic fracturing operations is available from NICNAS (2017c).



Figure 5-20 Cumulative frequency distribution of injected hydraulic fracturing volumes during 2014 in QLD across 7 production sites (based on data from APPEA).

The orientation of the fractured zone depends on the in-situ stress. In a homogeneous and isotropic medium, simple planar hydraulic fractures will grow oriented perpendicular to the minimum principal stress direction. In the production interval of Australian CSG wells, the minimum principal stress direction is typically horizontal therefore fractures will preferentially grow oriented vertically as depicted in Figure 5-21 (for further details, see Appendix 7). For this reason, a vertically-oriented rectangular fracture shape will be considered as one of the source zones for solute transport modelling.

Because of the dependency of the volume and shape of the hydraulic fracturing zone (i.e. the chemical source for transport simulations) on several parameters, several alternative source dimensions will be considered in the calculation of dilution and dispersion. The typical shape of the hydraulic fracturing zone of a vertical well is shown in Figure 5-21; fracture

treatments for Australian coal seams are designed and pumped to promote a fracture that will develop mainly in a vertical plane and have a length much greater than the height. Based on numerical modelling, estimates of the upper bound of horizontal hydraulic fracture growth are approximately 300 m (i.e. it is considered extremely unlikely a fracture would extend further than this distance from the well; for details, see Appendix 7).

For the purpose of solute transport modelling, the shape of the fractured zone will be simplified into a rectangle or a cube. The cube represents the condition where the fracture would extend equally far in all three directions; while this case is considered to have a low likelihood, it presents a useful comparison to the rectangular case as part of a sensitivity analysis. A rectangular-shaped fracture volume corresponds reasonably well with the theoretical fracture growth models discussed in Appendix 7 (e.g., Figure A7-1). The main difference with the theoretical model is in the tip of the fracture, which would not be accurately represented by a rectangular shape is preferred over other more complex structures because the analytical solutions used have limited flexibility in regards to source geometry representation. The sensitivity of use of different source geometries (i.e. cube or rectangle) will be discussed in the subsequent sections. As will become evident, for identical volumes of injected fluid, the difference in dilution/dispersion between different geometries is small; this demonstrates that the dilution is relatively insensitive to the geometry of the source, confirming the previous choice of a rectangular geometry. Three volumes for each shape will be considered: 0.5, 1, and 2 ML. In doing so, a realistic range of volumes site is considered in agreement with data presented in Figure 5-20; in this way the effect of using different injection volumes within and across sites is equally evaluated, albeit in a simplified manner.

The cube will have three different dimensions: 7.94 x 7.94 x 7.94 m³ (type C-1, 0.5 ML), 10 x 10 x 10 m³ (type C-2, 10³ m³ or 10⁶ L or 1 ML), and 12.6 x 12.6 x 12.6 m³ (type C-3, 2 ML). The rectangle will also have three different dimensions: 25 x 5 x 4 m³ (length x height x width) (type R-1, 0.5 ML), 50 x 10 x 2 m³ (type R-2, 1 ML), and 100 x 10 x 2 m³ (type R-3, 2 ML). The calculations assume, conservatively, that all hydraulic fracturing fluid remains in the subsurface. In this way the uncertainties about the fraction of hydraulic fracturing fluid that flows back to the surface as flowback and produced water is avoided.



Figure 5-21 Schematic of fracture zone for a vertical well (left). Cubic (middle) and rectangular (right) source zone used for transport modelling. Dimensions are not to scale.

The initial source concentration is set at a hypothetical value of 1. A schematic representation of the type C-1 source conditions and the calculated solute breakthrough curves at increasing distances from the source (downstream) is given in Figure 5-22. A summary of the calculated attenuation factors (DAF = 1/maximum concentration) is provided in Table 5-16 for the two source types (rectangular and cubic). Calculations will consider at least the following travel distances: 500 m, 1,400 m and 3,500 m (minimum, mean, and maximum particle travel distances from Table 2-24); intermediate distances will also be considered to obtain a more complete understanding of the effects of dilution and dispersion with increasing distances. Table 5-16 can be used as a simple screening tool in chemical risk and/or environmental impact assessments.

On the basis of these 3D solute transport calculations the process of dilution and dispersion will decrease any concentration from its initial value (here assumed 1 unit) down to 0.0011 units at a distance of 500 m from the source and further down to approximately 0.0002 units at a distance of 1,400 m from the source for the cubic source type C-2 (1 ML source volume). The resulting attenuation factors are (rounded) 900 and 4,400, respectively (Table 5-16). This decrease in concentration would apply for all the chemicals considered, in addition to the potential decrease in concentration due to degradation and sorption. The effect of dilution (here the value of 900 has been applied taking the 1 ML cubic source as the reference), together with effects of sorption and degradation on chemical concentration is shown in Table 5-17.



Figure 5-22 Application of 3D analytical solution to the advection-dispersion solute transport equation for the cubic source zone (type C-2). A: Conceptual model of perforated CSG well with fracturing fluid soon after injection; B: Source zone geometry; C: Solute breakthrough curves at 50, 100, and 200 from the source. Particle velocity v = 0.14 m/day.

Under the conditions that resulted in the relative concentrations at receptor in Table 5-17, the maximum distance travelled for the various compounds is very small: from 1 m for naphthalene and limonene using their maximum retardation factors (R = 432) to 493 m for bronopol using its minimum retardation factor ($R_f = 1.01$). Also Table 5-17 can be used as a simple screening tool in chemical risk and/or environmental impact assessments.

Source Type (volume)		Dilution Attenuation Factor as function of travel distance											
	200 m	300 m	400 m	500 m	1,000 m	1,400 m	2,000 m	3,400 m					
R-1 (0.5 ML)	400	782	1,240	1,770	5,180	8,690	15,000	33,300					
R-2 (1 ML)	189	378	605	866	2,560	4,310	7,440	16,600					
R-3 (2 ML)	84	177	290	419	1,260	2,130	3,690	8,280					
C-1 (0.5 ML)	421	807	1,270	1,800	5,240	8,730	15,020	33,500					
C-2 (1 ML)	213	406	638	903	2,620	4,370	7,510	16,700					
C-3 (2 ML)	108	205	321	454	1,310	2,190	3,760	8,370					

Table 5-16 Calculated Dilution Attenuation Factors due to dilution and dispersion as function of travel distance for rectangular (R-1, R-2, and R-3) and cubic (C-1, C-2, and C-3) source types. Values are rounded to three significant figures.

Table 5-17 Calculated relative concentration at receptor when all three attenuation processes are accounted for: chemical/biological degradation, sorption, and dilution/dispersion (cubic source C-2, 1 ML). Results are for a minimum travel time of 10 years (travel time class # 1 Table 2-24). MCI = Methyl-chloro-isothiazolinone. Initial source concentration is 1 (no units specified). ($f_{OC_r} = 0.001$). Underlined numbers have their concentrations decreased compared to calculations without sorption. When two numbers are shown results represent minimum/maximum R_t values.

		receptor: minimum travel time					
	A	naerobic	Ae	robic	Hydrolysis		
Chemical substance	Min Max		Min	Max	Min	Max	
2-methylphenol	0	<u>9.3E-5/ 1.1E-7</u>	0	0	1.1E-3	1.1E-3	
Naphthalene	0	1.1E-3	0	<u>0</u>	1.1E-3	1.1E-3	
Limonene	1.1E-3 1.1E-3		0	0	1.1E-3	1.1E-3	
НМХ	0	0	0	0	0	0	
2-butoxyethanol	0	0	0	<u>0</u>	1.1E-3	1	
Bronopol	1.1E-3	1.1E-3	1.1E-3	1.1E-3	0	<u>0</u>	
MCI	0 0		0	0	0	0	
Acrylamide polymer	1.1E-3	1.1E-3	1.1E-3	1.1E-3	1.1E-3	1.1E-3	

5.2.1.4. Summary of attenuation potential for organic compounds

In the above analysis of attenuation potential as a result of chemical/biological degradation, sorption, and dilution/dispersion, no explicit link was made with the various hydrostratigraphic layers relevant to the Gunnedah Basin. In the subsequent discussion the generic findings from the previous section are translated into layer-specific attenuation potential, expressed by the compound-specific Dilution Attenuation Factor (DAF). DAF values in Table 5-18 were obtained by consideration of the layers' organic carbon content as a key factor in determining sorption, the half-life values selected in Table 4-5, and the dilution/dispersion effect based on a minimal transport distance of 0.5 km for the Namoi alluvium, Pilliga Sandstone, and Blythesdaly Group, and a transport distance of 3.4 km for the deeper Maules Creek Formations (upper, Bohena coal measures, and lower). The 3.4 km transport distance for the Maules Creek Formations was the largest distance evaluated in section 2.6.4.4; this value is still very conservative as transport pathways within the Bohena coal measures are extremely long (see Section 2.6.4.3.2).

Table 5-18 Table of Dilution Attenuation Factors (DAF) for Gunnedah basin geology accounted for combined effect of chemical/biological degradation, sorption, and dilution/dispersion (organic chemicals). A = 2-methylphenol, B = Naphthalene, C = d-Limonene, D = HMX, E = 2-butoxyethanol, F = Bronopol, G = Methylchloroisothiazolinone, H = Acrylamide polymer. For effect of chemical/biological degradation, see layer-specific half-lifes in Table 4.5. For sorption effect layer-specific fo_{C_r} values were used (fraction of organic carbon × scaling factor). For effect of dilution/dispersion a 1 ML injection volume and travel distance of 0.5 km was used for Namoi alluvium, Pilliga Sandstone, and Blythesdale Group; 3.4 km distance was used for all three Maules Creek Formations. Colour codes are as follows: $DAF \le 10^3$; green; $10^3 \le DAF < 10^6$: orange; $DAF \ge 10^6$: blue.

Geology	<i>f</i> _{OC_r} (g/g)	_r (g/g) Dilution Attenuation Factor (DAF)							
		А	В	С	D	E	F	G	Н
Namoi alluvium	f _{oc_r} = 0.001	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	9.03E+02
Pilliga Sandstone	<i>f</i> _{OC_r} = 0	5.64E+03	9.03E+02	9.03E+02	1E+10	1E+10	1E+10	1E+10	9.03E+02
Blythesdale Group	f _{oc_r} = 0.0008 (rounded to 0.001)	1.07E+04	9.03E+02	9.03E+02	1E+10	1E+10	1E+10	1E+10	9.03E+02

Hoskisson seam	f _{oc_r} = 0.275	9.88E+08	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04
Maules Creek Formation (upper)	<i>f</i> _{OC_r} = 0	1.04E+05	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04
Maules Creek Formation (Bohena coal measures)	f _{oc_r} = 0.275	9.88E+08	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04
Maules Creek Formation (lower)	<i>f</i> _{OC_r} = 0	1.04E+05	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04

To aid with the interpretation of the magnitude of the DAF values, three classes were considered and values in Table 5-18 were colour coded accordingly:

- Class 1: DAF $\leq 10^3$. Such values would typically reduce concentrations from g/L to milligram/L (DAF = 10^3).
- Class 2: $10^3 \le DAF < 10^6$. Such values would typically reduce concentrations from g/L to microgram/L (DAF = 10^6).
- Class 3: DAF ≥ 10⁶. Such values would typically reduce concentrations from g/L to nanogram/L (DAF = 10⁹) or lower.

The above DAF classes (incorporating effects of all three attenuation processes), together with DAF values from Table 5-16 (only dilution/dispersion as attenuation process) represent a simple and cost-effective approach to a high-throughput screening process that could initially be used prior to undertaking more detailed hydrostratigraphically informed analyses. Its use, however, does require sufficient hydrostratigraphical and hydrochemical information to ascertain that the above DAF values are indeed applicable.

5.2.1.5. Multiple-well releases and cumulative effects

Hydraulic fracturing fluids released from multiple wells may lead to so-called cumulative effects; when chemicals are injected from different CSG wells, concentrations in groundwater may increase because of the principle of additivity. The exact magnitude of the combined concentration downstream from a well field will depend on several factors, including groundwater flow direction and rate, spacing between the wells, and positioning of the wells with respect to the main groundwater flow direction. A qualitative analysis is undertaken to explore if cumulative effects could exist, and if so, how important it could be.

The potential cumulative effects from multiple CSG wells were explored using the particle tracking analysis undertaken for the Gunnedah Basin (Pilliga Sandstone, see Figure 5-23). The results are repeated here with a focus on the receptors closest to the NPGA; these receptors did have pathways into the area with potential CSG wells. Backtracking particle analysis is used, with multiple particles (i.e. 9) released for each receptor. In doing so, more pathways can be explored than when a single particle is used, as small changes of the location of the starting position of the particle may result in a different pathway. Figure 5-23 shows multiple pathways that converge around a few grid cells that could contain CSG wells. Most pathways end up in a single cell that was found to have a high recharge value. In other words, the blue-

coloured cells are high recharge zones where water replenishes the groundwater; groundwater flow would naturally be from those recharge cells towards areas with lower hydraulic head: this can be a surface water feature, a groundwater dependent ecosystem, or a water bore. The observation that most receptors are connected to a small recharge area indicates that, at most, a couple of CSG wells (at most 3) could contribute to a minor accumulation effect (the actual effect depends on the distance to the source: as soon as the distance between multiple sources and receptor becomes more than 3 km [based on Table 5-16], dilution is sufficiently large to neutralise accumulation effects). This should not be of concern, as the dilution factors are very large making the groundwater system fairly robust to cumulative effects.



Figure 5-23 Calculated particle pathlines in Pilliga Sandstone show receptors-sources connections. Backward partical tracking with 9 particles released per receptor.

5.2.2. Inorganic substances

5.2.2.1. Attenuation due to dilution, dispersion and sorption

Inorganic substances do not degrade (unless by radioactive decay), hence the attenuation models (Equation 10) used for organics cannot be used for inorganics. Therefore the 3D analytical solution of Leij and Bradford (1994) was applied to derive DAF values due to dilution and dispersion. Model assumptions were the same as those used in Section 5.2.1.3. In terms of the particle velocities, maximum values from the Pilliga Sandstone were used as this would result in the fastest transport and hence earliest arrival in a receptor; this approach is conservative. Note that the geogenic inorganic elements As, Ba, and U present in the coal seam formations are assumed to migrate mainly within the coal seam formations. As the coal seam formations investigated here (i.e. Maulus Creek in Gunnedah and Walloon Coal Measures in Surat) have much lower particle velocities than the values used from the Pilliga Sandstone, the migration within the coal seam formations would be further retarded.

Figure 5-24 illustrates the effect of increasing travel distance on barium concentrations: for a receptor at a distance of 50 m the dilution is about 20, while at 500 m the dilution increases to 903. The effect of increasing sorption is also shown: at 500 m and with mild sorption (R = 4.2) the breakthrough curve is later compared to the simulation without sorption (R = 1). The maximum concentrations are identical for both $R_f = 1$ and $R_f = 4.2$.

A full analysis of the effects of sorption and dilution/dispersion for two travel distances is shown for barium in Figure 5-25. Sorption results in solute retardation which is responsible for delaying the arrival time of the solute at a given receptor; for

barium weak sorption results in arrival times from a few decades (receptor at 500 m) to a few hundred (receptor at 3,500 m) of years. For strong sorption (R = 2,625), the arrival times now become verly large, from several tens of thousands of years to hundreds of thousands of years. Dilution and dispersion, on the other hand, has the effect of reducing the concentration, with more dilution at greater travel distances.

DAF values are calculated for all inorganic elements considering a travel distance to a receptor equal to 500 m and minimum and maximum sorption values (Table 5-19). As discussed above, sorption does not affect the maximum concentration at the receptor. Sorption is important, however, in determining the travel time to reach the receptor.



Figure 5-24 Calculated barium concentrations (C/C₀) remaining at receptors (at 50 and 500 m from source) with (retardation $R_{\rm f}$ = 4.2) and without (retardation $R_{\rm f}$ = 1) sorption.



Figure 5-25 Effect of retardation (Rt = 4.2 and Rt = 2625) and travel distance (500, 1400, and 3500 m) on barium concentrations at receptors.

Table 5-19 Sorption parameters K _d and retardation factor R _b , travel time from source to receptor (T _{max}), calculated maximum concentration (C _{max}) and DAF at
500 m downstream the solute source. Unit input concentration assumed. Attenuation due to sorption and dilution/dispersion (1 ML injection volume).

Element	K _d (L/kg)	R _f (-)	T _{max} (days)	T _{max} (years)	C _{max} (-)	DAF
Barium	0.2	4.2	1.4E+04	3.8E+01	0.0011	903
	164	2630	8.8E+06	2.4E+04	0.0011	903
Boron	0.03	1.48	4.9E+03	1.4E+01	0.0011	903
	0.22	4.52	1.5E+04	4.1E+01	0.0011	903
Uranium	5	81	2.7E+05	7.4E+02	0.0011	903
	5000	80000	2.7E+08	7.3E+05	0.0011	903
Arsenic	2.9	47	1.6E+05	4.3E+02	0.0011	903
	17.3	278	9.3E+05	2.5E+03	0.0011	903

For receptor distances of 1,400 and 3,500 m characteristics of the solute breakthrough at receptor are summarised in Table 5-20 and Table 5-21. DAF values have now increased to 4,400 and 16,700 for receptor distances of 1,400 and 3,500 m, respectively. Furthermore, as a general rule, peak concentrations will appear at receptors only after a very long travel time, mostly in excess of several hundred years (even when the lowest sorption parameters are considerd). The only exception is boron, whose peak concentration could potentially be observed at a 500 m receptor 51 years after injection.

Table 5-20 Sorption parameters K_d and retardation factor R_t , travel time from source to receptor (T_{max}), calculated maximum concentration (C_{max}) and DAF at 1400 m downstream the solute source. Unit input concentration assumed. Attenuation due to sorption and dilution/dispersion (1 ML injection volume).

Element	K _d (L/kg)	R _f (-)	$T_{\rm max}$ (days)	$T_{\rm max}$ (years)	C _{max} (-)	DAF
Barium	0.2	4.2	5.3E+04	1.4E+02	0.00023	4,400
	164	2,630	3.3E+07	9.0E+04	0.00023	4,400
Boron	0.03	1.48	1.9E+04	5.1E+01	0.00023	4,400
	0.22	4.52	5.7E+04	1.5E+02	0.00023	4,400
Uranium	5	81	1.0E+06	2.8E+03	0.00023	4,400
	5,000	80,000	1.0E+09	2.7E+06	0.00023	4,400
Arsenic	2.9	47	5.9E+05	1.6E+03	0.00023	4,400
	17.3	278	3.5E+06	9.5E+03	0.00023	4,400

Table 5-21 Sorption parameters K_d and retardation factor R_t travel time from source to receptor (T_{max}), calculated maximum concentration (C_{max}) and DAF at 3,500 m downstream the solute source. Unit input concentration assumed. Attenuation due to sorption and dilution/dispersion (1ML injection volume).

Element	K _d (L/kg)	R _f (-)	T _{max} (days)	T _{max} (years)	C _{max} (-)	DAF
Barium	0.2	4.2	1.5E+05	4.0E+02	5.9E-05	16,700
	164	2,630	9.1E+07	2.5E+05	5.9E-05	16,700
Boron	0.03	1.48	5.1E+04	1.4E+02	5.9E-05	16,700
	0.22	4.52	1.6E+05	4.3E+02	5.9E-05	16,700
Uranium	5	81	2.8E+06	7.7E+03	5.9E-05	16,700
	5,000	80,000	2.8E+09	7.6E+06	5.9E-05	16,700
Arsenic	2.9	47	1.6E+06	4.5E+03	5.9E-05	16,700
	17.3	278	9.6E+06	2.6E+04	5.9E-05	16,700

The resulting dilution factors are primarily applicable to the coal seam target formations (i.e. Hoskisson/Bohema seam and Maules Creek Formation in the Gunnedah Basin and Walloon Coal Measures in the Surat Basin), as these would be the main source of the elements As, Ba and U. For the element B (a hydraulic fracturing additive) there may potentially be pathways through shallower groundwater as a result of the leaky well pathways (Section 2.6.2). As unperturbed coal seam

formations exhibit reducing geochemical conditions, uranium is predominantly present as $U(IV) - dominated by the aqueous species U(OH)_4(aq) - which is not readily available for migration owing to its low solubility and high sorption (Ochs et al. 2015). For example, Ochs et al. (2015) recommended a <math>K_d$ value of 30,000 L/kg for U(IV) compared to 50 L/kg for U(VI) for a calcite dominated solid phase and a pore-water pH of 10. In other words, the higher K_d = 5,000 L/kg for U is probably more representative for such deep groundwater conditions than the low K_d = 5 L/kg.

5.2.3. Linking spatial analysis and DAF values

In a final analysis, the frequency distributions displaying proximity between CSG wells and specific receptors are combined with compound-specific DAF values (e.g. Table 5-18) to attribute a likelihood to the various DAF values. The procedure is illustrated for 2-methylphenol in Figure 5-26. Note that these results are for the Gunnedah Basin; similar results can be obtained for the Surat Basin (see Section 5.3.3). From the particle tracking analysis in the Gunnedah Basin the minimum, mean, and maximum travel time between receptors in the Pilliga Sandstone and CSG wells with plausible pathways into the Pilliga Sandstone were found to be 10 years (3,660 days), 34 years (12,300 days), and 92 years (33,500 days) for the < 100 year travel class (see Table 2-24). For each of these travel times a DAF value was calculated (Figure 5-26):

- For travel time *t* = 10 years: DAF = 6.2 if only chemical/biological degradation and sorption is accounted for and DAF = 5.64E3 when also dilution/dispersion is accounted for,
- For travel time *t* = 34 years: DAF = 475 if only chemical/biological degradation and sorption is accounted for and DAF = 2.08E6 when also dilution/dispersion is accounted for, and
- For travel time t = 92 years: DAF =1.85E+7 if only chemical/biological degradation and sorption is accounted for and DAF > 1E10 when also dilution/dispersion is accounted for.

For these travel times, also the linear distance between the CSG well and specific receptor is known: in this case these are 0.5, 1.4, and 3.5 km. In other words, one now has the following data sets: {DAF=5.64E3, 0.5 km}, {DAF=2.08E6, 1.4 km}, and {DAF = >1E10, 3.5 km}. From the frequency-proximity curve, the likelihood for the proximities 0.5, 1.4, and 3.5 km can be derived. These are 0.015%, 0.04%, and 0.25%; note these probabilities represent probability of non-exceedance. This means that the probability of having a DAF value less than or equal to 5.64E3 is 0.015%, whereas the probability of having a DAF value less than or equal to 5.64E3 is 0.015%, whereas the probability of having a DAF value less than or equal to 1E10 is 0.25%. Or, conversely, the probability of having a DAF value larger than 5.64E3 is 100-0.015 = 99.985% and the probability of having a DAF value larger than 1.E10 is 100 - 0.25% = 99.75%. Clearly, the higher DAF values are much more likely than the small DAF values. Similar analyses can be undertaken for the other assets and other chemicals.

The overall conclusion from the Level-2 analysis is that all the selected organic and inorganic chemicals exhibit large to very large DAF values, with the lowest calculated DAF values (around 900) having a very low probability of non-exceedance of less than one tenth of a percent (i.e. 0.015%, based on the data shown in Figure 5-26). In other words, there is a 0.015% chance of finding DAF values smaller than 900 in the case study area (a very small chance indeed). Conversely, there is a 99.985% chance (100% - 0.015%) that DAF values in excess of 900 will be encountered in the case study area. In conclusion: a DAF value as low as 900 is very rare (i.e. unlikely) in the study area; an overwhelming majority of DAF values will be much larger.

Even the largest calculated DAF values (> 10^{10}) are applicable to more than 99.75% (100% - 0.25%) of the water bores; in fact, because 99.75% of CSG well-water bore distances are larger then 3,4 km, many water bores will have DAF values in excess of 10^{10} (based on the data shown in Figure 5-26).

DAF values for other hydrostratigraphic units within the test case area of the Gunnedah Basin will at least have the same magnitude or higher because their travel times are much longer (see Table 2-23). Even when the proximity-frequency relationships for different receptors yield higher probabilities for shorter travel distances, the very large DAF values will guarantee that the overall risk for exposure to unacceptable concentrations remains low. Use of these DAF values in other sedimentary basins is discussed in Section 5.6.3.



Figure 5-26 Combination of frequency distribution of proximities (distance between CSG well and receptor) and DAF values for 2-methylphenol. Right panel shows DAF values based on chemical/biological degradation and sorption only (top) and DAF values accounting for all three attenuation processes (chemical/biological degradation and dilution/dispersion). DAF values representative for Pilliga Sandstone conditions.

5.3. Application to Surat Basin

5.3.1. Organic substances

5.3.1.1. Attenuation due to chemical/biological degradation

As demonstrated in Section 5.2.1.1, the two key parameters that govern chemical/biological degradation are the compounds' half-life and the travel time from source to receptor. Relevant half-lifes for the Surat Basin hydrostratigraphic units were discussed in Table 4-6. For reasons of conservatism (transport distance to receptors are much larger in the Surat Basin compared to those in the Pilliga Sandstone), the generic results based on a minimum travel time (Table 5-2) were used to derive layer-specific dilution values (see Table 5-22). As a result, the attenuation values derived for the Surat Basin will be at least as large as those for the Gunnedah Basin.

5.3.1.2. Attenuation due to chemical/biological degradation and sorption

In a second series of calculations both chemical/biological degradation and sorption was considered. The compoundspecific partition coefficients K_d used for the Surat Basin (Table 5-9) were derived based on compound-specific baseline K_{OC} values and the fraction of organic carbon (for f_{OC_r} values, see Table 5-8). As with the chemical/biological degradation, effect of sorption for specific hydrostratigraphic layers was obtained on the basis of the generic calculations (Section 5.2.1.2).

5.3.1.3. Attenuation due to dilution and dispersion

The final and third attenuation process that will be included is the attenuation due to dilution and dispersion in groundwater. The methodology applied to the Gunnedah Basin will equally be applied to the Surat Basin layers. For reasons of conservatism (transport distances to receptors are much larger in the Surat Basin compared to those in the Pilliga Sandstone), the generic results based on a Pilliga Sandstone travel distances (from 0.5 to 3.4 km) will be used here. For final results, see Table 5-22.

5.3.1.4. Summary of attenuation potential for organic compounds

The layer-specific attenuation potential, expressed by the compound-specific Dilution Attenuation Factor (DAF) values, are summarised in Table 5-22. These values were obtained by consideration of the layers' organic carbon content as a key factor in determining sorption, the half-life values selected in Table 4-6, and the dilution/dispersion effect based on a minimal transport distance of 0.5 km for the Dawson River alluvium, BMO Group, and Gubberamunda, and a transport distance of 3.4 km for the deeper Springbok Sandstone, Walloon Coal Measures and Hutton Sandstone. The 3.4 km transport distance for the last three formations was the largest distance evaluated in section 5.2.1.3; this value is still very conservative as transport pathways within these formations are considerable longer, i.e. on average 10 km for Springbok Sandstone, 11 km for the Walloon Coal Measures, and 33 km for the Hutton Sandstone (see Table 2-26).

Table 5-22 Table of Dilution Attenuation Factors (DAF) for Surat basin geology accounted for combined effect of chemical/biological degradation, sorption, and dilution/dispersion (organic chemicals). A = 2-methylphenol, B = Naphthalene, C = d-Limonene, D = HMX, E = 2-butoxyethanol, F = Bronopol, G = Methylchloroisothiazolinone, H = Acrylamide polymer. For effect of chemical/biological degradation, see layer-specific half-lifes in Table 4.6. For sorption effect layer-specific foc_r values were used. For effect of dilution/dispersion a 1 ML injection volume and travel distance of 0.5 km was used for Dawson River alluvium, BMO Group, and Gubberamunda Sandstone; 3.4 km distance was used for all subsequent layers. Colour codes are as follows: DAF $\leq 10^3$: green; $10^3 \leq$ DAF $\leq 10^6$: orange; DAF $\geq 10^6$: blue.

Geology	<i>f</i> oc_r (g/g)			Dilution /	Attenuatio	on Factor	(DAF)		
81		A	В	С	D	E	F	G	Н
Dawson River alluvium	f _{oc_r} = 0.001	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	1E+10	9.03E+02
Bungil Formation- Mooga Sandstone- Orallo Formation (BMO Group)	<i>f</i> _{OC_r} = 0	5.64E+03	9.03E+02	9.03E+02	1E+10	1E+10	1E+10	1E+10	9.03E+02
Gubbera- munda Sandstone	f _{oc_r} = 0.0008 (rounded to 0.001)	1.13E+04	9.03E+02	9.03E+02	1E+10	1E+10	1E+10	1E+10	9.03E+02
Westbourne Formation	<i>f</i> _{OC_r} = 0	1.05E+05	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04
Springbok Sandstone	<i>f</i> _{OC_r} = 0	1.05E+05	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04
Walloon Coal Measures	f _{oc_r} = 0.0126	3.36E+08	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04
Hutton Sandstone	$f_{OC_r} = 0$	1.05E+05	1.67E+04	1.67E+04	1E+10	1E+10	1E+10	1E+10	1.67E+04

5.3.2. Inorganic substances

The analysis undertaken for the Gunnedah Basin can be used as a guide to infer contaminant behaviour in the Surat Basin. Based on considerations in Section 4.4.1.1 in regards to the lack of information to derive basin specific partition coefficients K_d , the same K_d values will be used for Surat and Gunnedah Basin. As the discussion in Section 5.2.2.1 highlighted, the main parameter determining the degree of dilution is the travel distance (i.e. distance between chemical source and receptor). The retardation factor R_f , which determines the chemical's travel velocity, does not affect the dilution but does determine the arrival time of the maximum concentration.

Given these conditions, the analysis here will be limited to an assessment of the effects of very low pore-water velocity v derived for the Walloon Coal Measures based on the particle tracking analysis (Section 2.6.5.4), i.e. on average $v = 4.6 \times 10^{-4}$ m/day, or 300 times slower than the value of 0.14 m/day used for the Gunnedah Basin. For the Gubberamunda Sandstone aquifer of the Surat Basin, similarly low velocities were derived (i.e. between $v = 3.71 - 6.13 \times 10^{-4}$ m/day) (Table 2-27).

Therefore, the subsequent discussion for the Walloon Coal Measures is also representative for the Gubberamunda Sandstone aquifer.

The pore-water velocity v does affect, however, the dispersion coefficients D, given that $D = \lambda \times v$. Using the same dispersivity as for the Gunnedah calculations ($\lambda_L = 7.14$ m), the dispersion coefficients for the Surat become as follows: $D_L = 4.6 \times 10^{-4} \times 7.14 \text{ m}^2/\text{day} = 3.3 \times 10^{-3} \text{ m}^2/\text{day}$, and $D_{TH} = D_{TV} = 3.3 \times 10^{-4} \text{ m}^2/\text{day}$. Although the dispersion coefficients for the high (Gunnedah Basin) and low (Surat Basin) velocity values are different, their so-called Peclet Number (Pe) is identical:

$$Pe = \frac{vL}{D} = \frac{0.14x500}{1} (Gunnedah) = \frac{0.00046x500}{0.0033} (Surat) = 70$$
(18)

where v and D are as defined previously and L is transport distance (here assumed 500 m). Peclet Numbers are used to determine the relative contribution of advection over dispersion to solute transport (Huysmans and Dassargues 2005). Values of Pe smaller than 1 indicate solute transport over the distance L is dominated by dispersion, whereas Pe values larger than 10 are characteristic of advection-dominated systems (Mazurek et al. 2011). The calculated Peclet Number of 70 (equation 18) indicates solute transport is dominated by advection. This is further demonstrated in Figure 5-27a, where the dispersion-velocity relationship is depicted for three values of the (longitudinal) dispersivity parameter ($\lambda_L = 0.714$, 7.14, and 71.4 m). These relationships are plotted against a background of three characteristic transport systems: a dispersion dominated system for Pe \leq 1 (coloured blue), an advection dominated system with Pe \geq 10 (coloured green), and a transition zone with 1 \leq Pe \leq 10 (coloured white).

Using the dispersion coefficients D_L of 1 and 0.0033 m²/day, the solute migration was calculated for a receptor at 500 m while neglecting sorption (R = 1) as the sole purpose of the calculation was to understand the effect of a reduced dispersion (which is independent of R). Solute breakthrough for a high velocity and low velocity environment are compared in Figure 5-27b; as expected, the breakthrough is later under the conditions of a lower velocity. More importantly, because of the very low dispersion coefficients used in both simulations (i.e. both $D_L = 1$ and 3.3×10^{-3} m²/day are considered small relative to the travel distance of 500 m), the effect of dispersion is nearly identical hence the peak concentrations are nearly identical. As was evident from Figure 5-27a, both the low and high velocity cases have a high and identical Pe = 70, which clearly falls within the advection dominated system. Under those conditions, the effect of dispersion on decreasing solute concentrations is identical for both velocities. Note that the advection-dispersion solute transport (equation 15 and 16) can be written in dimensionless form, in which case the Peclet Number becomes the only parameter determining solute distribution in space and time (Toride et al. 1999; van Genuchten et al. 2012).



Figure 5-27 A: Relationship between velocity and dispersion coefficient for different values of dispersivity λL . Blue coloured area indicates dispersion dominated transport (Pe ≤ 1); green coloured area indicates advection dominated transport (Pe ≥ 1). B: Barium concentrations at a 500 m receptor using high velocity (0.14 m/day) and low velocity (3.3×10⁻³ m/day). Sorption is not considered (R=1).

Note that use of small dispersion values is conservative; indeed, the larger the dispersion the larger the solute spreading and hence the smaller the peak concentration.

These analysis indicate that, for the same travel distance between source and receptor as considered for the Gunnedah Basin calculations, dilution in the Surat Basin Walloon Coal Measures is at least as high. Therefore, the dilution factors derived for the Gunnedah Basin can be used as guide values for the Surat Basin. Use of these DAF values in other sedimentary basins is discussed in Section 5.6.3.

5.3.3. Linking spatial analysis and DAF values

In the same way as was done for the Gunndah Basin, the frequency distributions displaying proximity between CSG wells and specific receptors are combined with compound-specific DAF values to attribute a likelihood to the various DAF values (Figure 5-28). The procedure is again illustrated for 2-methylphenol; the DAF values are the same as those for the Pilliga Sandstone (based on analysis in Sections 5.3.1.1 to 5.3.1.4). The only difference is with the distance-proximity data, which are specific to the Surat Basin (based on analysis in Section 3.3). From the cumulative probability curve, the likelihood (i.e. probability of non-exceedance) for the proximities 0.5, 1.4, and 3.5 km was derived to be 0.05%, 0.4%, and 2%, respectively. This means that the probability of having a DAF value less than or equal to 5.64E3 is 0.5%, whereas the probability of having a DAF value less than or equal to 1E10 is 2%. Or conversely, the probability of having a DAF value larger than 5.64E3 is 100-0.015 = 99.985% and the probability of having a DAF value larger than 1.E10 is 100 – 0.25% = 99.75%. Clearly, the higher DAF values are much more likely than the small DAF values. Similar analyses can be undertaken for the other assets and other chemicals.



Figure 5-28 Combination of frequency distribution of proximities (distance between CSG well and receptors: stock and domestic bores, left panel) and DAF values for 2-methylphenol. Right panel shows DAF values based on chemical/biological degradation and sorption only (top) and DAF values accounting for all three attenuation processes (chemical/biological degradation and sorption and dilution/dispersion). DAF values representative for BMO Group conditions (from Table 5-22).

DAF values previously derived for the Pilliga Sandstone are used as guide values for the Surat Basin (Table 5-22). This is based on findings that dilution in the Surat Basin Walloon Coal Measures and aquifers such as the Gubberamunda Sandstone aquifer and the BMO group aquifer is at least as high as considered for the Gunnedah Basin calculations.

The overall conclusion from the Level-2 analysis is that all the selected organic and inorganic chemicals exhibit large to very large DAF values, with the lowest calculated DAF values (around 900) having a very low probability of less than one tenth of a percent (i.e. 0.05%, based on the data shown in Figure 5-28). Even the largest calculated DAF values (> 10¹⁰) still have a high probability of exceedance, i.e. more than 98% of the water bores will have DAF values in excess of 10¹⁰ (based on the data shown in Figure 5-28).

DAF values for other hydrostratigraphic units within the test case area of the Surat Basin will at least be as large or larger than in those of the Pilliga Sandstone Gunnedah sedimentary Basins (see Table 5-22). Even when the proximity-frequency relationships for different receptors yield higher probabilities for shorter travel distances, the very large DAF values will guarantee that the overall risk for exposure to unacceptable concentrations remains low.

5.4. **Conclusions for Level-2 analysis**

Specifically, the conclusion for the chemicals selected here for the proof-of-concept-testing is:

- For typical hydraulic fracturing and drilling chemicals:
 - bronopol, methyl-chloro-isothiazolinone: chemicals are unlikely to pose a risk of adverse health effects (based on long-term public exposure) NICNAS (2017b). The NICNAS (2017b) assessment of surface and shallow groundwater risks remains valid for deeper groundwater related risks, as both chemicals have very large DAF values of 10¹⁰ or larger, which is sufficiently large to reduce initial source concentrations to levels 'of low concern'.
 - boron (boric acid, borax): chemical of potential concern (a potential risk of adverse health effects in case of long-term public exposure) based on the assessment of surface and shallow groundwater risks (NICNAS 2017b). Under the conditions of this study any boron moving from deeper groundwater to a receptor is likely to be diluted sufficiently to reduce concentrations to below guideline values (also see Table 5-24).
 - *limonene:* this chemical could not be assessed based on the Inventory Multi-tiered Assessment and Prioritisation Framework (NICNAS 2015). With DAF values ranging from 900 up to 10¹⁰ (depending on hydrostratigraphy), the current analysis indicates that it is very likely that attenuation for limonene would be sufficient to reduce its concentrations to levels 'of low concern',
 - acrylamide polymer: this chemical represents an important group of polymers used in hydraulic fracturing and that are of low concern for human health (NICNAS 2017b) and the environment (DoEE 2017b). Based on DAF values ranging from 900 up to 16,700 (depending on hydrostratigraphy), the current analysis indicates that it is very likely that attenuation for acrylamide polymer would be sufficient to reduce its concentrations to levels 'of low concern'.
- Explosives (*HMX*): because this chemical has a very large DAF values of 10¹⁰ or larger, this is considered sufficiently large to reduce initial source concentrations to levels 'of low concern'.
- Geogenics: 2-methylphenol, naphthalene, uranium, arsenic, and barium. Based on the same reasoning as the previous chemicals, a sufficient dilution can be obtained to reduce concentrations to levels 'of low concern' (also see Table 5-25).

5.5. Mixed toxicity

This study only considers the toxicity of chemicals in isolation, whereas in the deeper groundwater and potentially in connected surface water environments organisms may be exposed to several different chemicals at the same time as a result of drilling and/or hydraulic fracturing. This could potentially be true for drilling or hydraulic fracturing fluids where several chemicals are combined in the fluid mix or are injected one after the other. For instance, Santos reports 18 chemicals present in its Scotia drilling fluids (Santos 2016). Hydraulic fracturing fluids reported by Halliburton (2014) had up to 21 different chemicals.

It was beyond the scope of this study to look at how components in a mixture may interact and what effect this can have on organisms in the environment when they are exposed, simultaneously, to different chemicals. For a review of current approaches used to evaluate the effect of mixtures in order to understand how this impacts the assessment of risk that pollutants can pose to the environment, the reader is reffered to Hyes et al. (2016).

However, based on the assessments of attenuation, especially due to sorption onto organic matter and potentially on the rock and/or sediment matrix, there are some preliminary conclusions that can be made that allow to address the issue of mixed toxicity from the viewpoint of whether or not combined exposure to several chemicals is at all possible. Indeed, when different chemicals have different sorption coefficients (K_{OC}), their concentrations in groundwater will be spread differently, with those that have the lowest K_{OC} arriving first and those with the highest K_{OC} arriving last. This results in process similar to chromatographic separation, where chemicals flowing through a chromatographic column are separated based on their interaction with the column material.

For instance, taking the example of limonene and 2-butoxyethanol: the smallest K_{oc} for limonene is 1000 L/kg whereas that for 2-butoxyethanol is 3 L/kg (Table 4-4). Based on these values, limonene will travel about 350 times faster than 2-butoxyethanol. As a result, the maximum concentrations at any receptor will be separated in time such that any organism will not be exposed to the maximum concentration of both chemicals.

This very simplistic analysis can be done for any combination of chemicals to identify which chemicals might travel at a similar velocity, and hence identify groups of chemicals to which organisms may be exposed at the same time. Such information may guide an experimental programme in selecting a relevant mix of chemicals for testing.

5.6. **Applications with DAF values**

5.6.1. Significance of DAF values

The application of the combined attenuation processes, i.e. chemical/biological degradadion, sorption, and dilution/dispersion, results in large to very large dilution factors for deep groundwater. For all chemicals investigated, the overall minimum DAF value is just under 1,000 (i.e. 903), whereas most other values exceeded 10⁴ or even 10¹⁰ (Table 5-18 and Table 5-22). The significance of such large values is first illustrated on the basis of the ecotoxicity data from Table 5-23 and Table 5-24. Based on available data regarding concentrations of hydraulic fracturing chemicals after dilution but prior to injection (CPI) or concentrations of geogenic chemicals following interaction between coal samples and leaching fluids (CGL), and their corresponding predicted no effect concentrations (PNEC) (for ecosystem protection) and drinking water guideline value (for protection of human health, DWGV), the minimum DAF values were calculated that would ensure the PNEC and drinking water guideline values would not be exceeded, i.e. the risk quotion RQ = CPI (or CGL)/PNEC < 1. PNEC values are for chronic aquatic ecotoxicity and were calculated using toxicity test data such as LC50, EC50, other L(E)Cx values, NOEC (no observed effect concentration) and LOEC (lowest observed effect concentration) (Section 4.6 and DoEE 2017b). These PNEC values for aquatic ecotoxicity are very conservative since based on limited toxicity data requiring use of large assessment or safety factors.

Based on results from Table 5-23, the largest required DAF value for ecosystem protection is nearly 6,000 (for MCI) and 54 for protection of human health (boron). Due to lack of many PNEC and drinking water guide values, DAF values could only be calculated for a small number of chemicals. For the geogenic compound naphthalene, a recommended maximum drinking water concentration of 0.1 mg/L was proposed in the US by ATSDR (2005). Based on this value, no dilution or attenuation would be required to satisfly the condition RQ < 1. Note that DAF values in Table 5-23 (and Table 5-24 and Table 5-25) have no relationshp to any specific travel distance; the DAF values are simply calculated as CPI/PNEC or CGL/DWGV.

		Concentration	Ecosystem protection		Protection of human health	
CAS No.	CAS Chemical Name	prior to injection/ geogenic concentration (mg/L)	PNEC (mg/L)	Minimum DAF for RQ < 1	Drinking water guideline value (mg/L)	Minimum DAF for RQ < 1
95-48-7	2-methylphenol (o-cresol)	0.021ª	NR	NC	NR	NC
91-20-3	naphthalene	0.00006 ⁱ	0.016	0.004	NR	NC
138-86-3	limonene	94 ^b	NR	NC	NR	NC
2691-41-0	HMX	NR	NR	NC	NR	NC
111-76-2	2-butoxyethanol	40 ^c	0.165	242	NR	NC
52-51-7	bronopol	15 ^d	NR	NC	NR	NC
26172-55-4	MCI	4 ^b	0.00062 ^f	5,968	NR	NC
9003-05-8	acrylamide polymer	NR	NR	NC	NR	NC
#	boron (boric acid, H ₃ BO ₃)	216	0.83 ^g	260 ^g (45) ^h	4	54
#	uranium	0.018ª	0.0005	36	0.0017	11
			0.015	1.2	NR	NC
#	barium	1.1ª	NR	NC	2	0.6
		0.023ª	0.013 – As(V) ^e	2	0.01	2.3
#	arsenic		0.024 – As(III) ^e	1	NR	NC

Table 5-23 Predicted no effect concentrations (PNEC) for the protection of aquatic freshwater biota and drinking water guideline concentrations for Australia (NHMRC and NHMMC (2011), and minimum DAF to satisfy the condition RQ < 1. NR = not reported. NC = not calculated.

^a pH 7 leach test on coal samples (citrate added, a common constituent of hydraulic fracturing fluids): Apte et al. (2017a); ^b Santos (2014); ^c NICNAS (2017c); ^d Coordinator General (2010); ^e high reliability (ANZECC/ARMCANZ 2000); ^f (DoEE 2017b); ^g for B (boron); ^h for boric acid (=260/(61.8/10.8)); ⁱ Stearman et al. (2014).

The largest required DAF value for ecosystem protection, using data from Table 5-24, is approximately 2,500,000 (for hypochlorous acid, sodium salt). The next largest DAF value is approximately 600,000 (for carbonic acid, sodium salt). All other DAF values are smaller or much smaller. When only attenuation due to dilution and dispersion is considered, a condition which would be relevant for non-degrading organic compounds and inorganic chemicals, the minimum DAF value of around 900 was obtained for a travel distance of 0.5 km, while a DAF = 4,850 was obtained for a 1.5 km travel distance, and DAF = 13,800 for a 3 km travel distance (based on Table 5-26). The evidence from Table 5-24 shows that for most chemicals sufficiently large dilution values would be obtained to meet the requirement RQ < 1, within a travel distance of around 1 km, even without taking dilution within the receiving waterbody into account. Such information may be used to derive setback distances beyond which one may reasonably assume the combined attenuation processes would result in concentrations of hydraulic fracturing chemicals that would not cause a negative impact on human health and the environment.

Table 5-24 Selection of hydraulic fracturing chemicals with previously estimated concentrations prior to injection – CPI (NICNAS 2017c) and PNEC values for
aquatic ecosystem protection (DoEE 2017b). Minimum Dilution Attenuation Factor (DAF) was calculated as CPI/PNEC. #Na2CO3 - Alternative names: sodium
carbonate, soda ash: when dissolved in water, it forms carbonic acid (H2CO3) and sodium hydroxide (NaOH). @NaClO – althernative names: sodium
hypochlorite, chloride of soda, bleach: when dissolved in water, it forms chlorine and sodium hydroxide.

CAS No.	CAS Chemical Name	Conc. after Final Dilution Prior to Injection (mg/kg or mg/L)	PNEC (mg/L)	Minimum DAF for RQ < 1
107-21-1	1,2-Ethanediol	496	10	50
1310-73-2	Sodium hydroxide (Na(OH))	137.5	2.4	57
2682-20-4	3(2H)-Isothiazolone, 2-methyl-	1.1	0.0007	1,571
497-19-8	Carbonic acid sodium salt (1:2)#	2,532,000	4.24	597,170
55566-30-8	Phosphonium, tetrakis(hydroxymethyl)-, sulfate (2:1) (salt)	41.25	0.94	44
64-19-7	Acetic acid	525	15	35
67-63-0	2-Propanol	13.4	500	0.03
7447-40-7	Potassium chloride (KCl)	22,963	3.73	6,156
75-57-0	Methanaminium, N,N,N-trimethyl-, chloride (1:1)	1,273	4.62	276
7647-01-0	Hydrochloric acid	52.5	6.20	8
7681-52-9	Hypochlorous acid, sodium salt (1:1) [@]	57.7500	0.000023	2,510,870
7727-54-0	Peroxydisulfuric acid ([(HO)S(O) ₂]2O ₂), ammonium salt (1:2)	452.1	0.92	491
7786-30-3	Magnesium chloride (MgCl ₂)	3.4	2.12	2
77-92-9	1,2,3-Propanetricarboxylic acid, 2- hydroxy-	1,765	15.3	115
9000-30-0	Guar gum	2,600	0.22	11,927
7647-14-5	Sodium chloride	400	3.14	127

We next compare maximum concentrations of inorganic elements measured in laboratory tests where coal samples were subjected to acidic fluids to simulate effects of hydraulic fracturing fluids on release of inorganic elements (see Section 4.5) with their water quality guidelines for aquatic ecosystem protection. The minimum DAF value was calculated that would result in a risk quotiont RQ < 1 (Table 5-25). The largest required DAF value is 9,200 for lanthanum, with the next larger 2,600 for aluminium. In other words, for all inorganic elements, except lanthanum, a sufficiently large DAF value is obtained within a distance of 1.5 km travel distance (DAF = 4,850). This assessment does only account for dilution/dispersion; additional attenuation (e.g. due to sorption) is likely for most of these elements.

Table 5-25 Selection of trace elements measured in laboratory tests, guide values (NHMRC and NHMMC 2011), and minimum Dilution Attenuation Factor (DAF) required to achieve RQ < 1.

, and c	concentration	Minimum DA for RQ <1	
0.055	143	2600	
9	1.51	0.2	
13	23	2	
0.13	13	100	
370	617	2	
0.2	33	165	
1	134	134	
1.4	36	26	
1.4	196	140	
18	65	4	
0.04	368	9200	
3.4	1648	485	
1.7	21	12	
34	6.4	0.2	
11	35	3	
5	11	2	
0.03	4.2	140	
3	0.68	0.2	
0.5	18	36	
6	370	62	
8	595	74	
	 0.055 9 13 0.13 370 0.2 1 1.4 1.4 1.4 1.8 0.04 3.4 1.7 34 1.1 5 0.03 3 0.5 6 8 	valueconcentration0.05514391.5113230.13133706170.2331.4361.41961.4650.043683.416481.721346.411355110.034.230.680.51863708595	

In a final analysis a relationship is derived between the travel distance or setback distance that is required to achieve a given DAF value, considering only dilution and dispersion as attenuation processes (Figure 5-29). The setback distance is the minimal distance between a CSG well and a receptor that is considered sufficient to reduce the chemical concentration to values below regulatory limits or no-effect levels, without taking dilution within the receiving waterbody into account. Note this is an example only; actual values for setback distance would need to be developed based on site-specific circumstances. The relationships depicted in Figure 5-29 are derived for different source geometries and volumes of injected fluids; the first set of relationships are without consideration of degradation and sorption (Figure 5-29a). The relationships further show how dilution increases as additional attenuation due to degradation (Figure 5-29b) and both degradation and sorption are accounted for (Figure 5-29c and d). Because differences between the cubic (C-1, C-2, and C-3)

and rectangular (R-1, R-2, and R-3) sources are negligible (Table 5-16), the cubic source C-2 (1ML injected volume) is used for exploring the effects of degradation (Figure 5-29b) and sorption on attenuation (Figure 5-29c and d).

In terms of source volume, as expected, the larger the injected volume of fracturing fluids, the smaller the dilution (Table 5-16). Each time the volume is doubled, the dilution factor is decreased by a factor two. Given the flow conditions of these simulations, the dilution is not sensitive to the geometry of the plume; the much more elongated rectangular plumes produce nearly the same dilution, certainly at distances larger than 1 km. When an initial plume height of 5 m (the mimimum height considered) or 2 m wide (the minimum width considered) is used, its concentration at the centre of the plume does not differ from that when a $10 \times 10 \times 10 \text{ m}^3$ cube is used.

Incorporating degradation into the advection dispersion solute transport model has a large effect on the DAF values; for instance, at 2 km distance the DAF value increases from 7,500 without degradation to 270,000 with degradation (example half-life $T_{1/2} = 1,386$ days). For a half-life $T_{1/2} = 693$ days the DAF value becomes 3×10^8 (Figure 5-29b).

Even larger DAF values are obtained when subsequently sorption is accounted for. Compared to the DAF value of 7,500 (without sorption and half-life $T_{1/2}$ = 1,386 days), taking the retardation factor R_f = 2 increases the DAF value to 3×10⁸ (Figure 5-29c). If the half-life $T_{1/2}$ = 693 days, the DAF value becomes 5×10¹⁴ (Figure 5-29d).



Figure 5-29 Dilution attenuation factor (DAF) in function of travel distance or setback distance (this is an example only; actual values would need to be developed based on site-specific circumstances). (A) Dilution and dispersion without degradation and without sorption. Closed circles are calculated; coloured lines are fitted. Cubic source types are C-1 (0.5 ML), C-2 (1 ML) and C-3 (2 ML); open circles are for rectangular source types R-1, R-2 and R-3. (B) Dilution, dispersion and degradation for cubic source type C-2. (C) Dilution, dispersion, degradation and sorption for cubic source type C-2 (half-life $T_{1/2}$ = 1,386 days). (D) Dilution, dispersion, degradation and sorption for cubic source type C-2 (half-life $T_{1/2}$ = 693 days).

For many chemicals the relationship in Figure 5-29a is a conservative estimate that can be used if no site-specific information on sorption and degradation is available. The data from Figure 5-29a are also provided in Table 5-26 (for the cubic C-1, C-2, and C-3 source types). For an injection volume of 0.5 ML a setback distance of 2 km would satisfy all but two of the DAF criteria from Table 5-24 (organic and inorganic hydraulic fracturing chemicals) and Table 5-25 (geogenics) (the exception being hypochlorous acid and carbonic acid sodium salt).

It is important to note that the injection volumes in Table 5-26 each have an estimated probability of occurrence, based on current industry practice (see discussion in Section 5.2.1.3). The 0.5 ML injection volume has a probability of non-exceedance of 18%: 18 times out of 100 a smaller volume is used, or conversely, 82 times out of 100 a larger volume is used. The 1ML injection volume has a probability of non-exceedance of 66%: 66 times out of 100 a smaller volume will be used, while in 34 times out of 100 a larger volume is used. Finally, the 2 ML injection volume has a probability of non-exceedance of 99%: 99 times out of 100 a smaller volume will be used, and only in one out of 100 times a larger volume.

Table 5-26 Setback distances to obtain minimum DAF values for which RQ < 1 (attenuation based on dilution and dispersion only, source type C-1, C-2, and C-3). Injected volumes in megalitres (1 ML = one million litres). This is an example only; actual values would need to be developed based on site-specific circumstances.

Setback distance (km)	DAF C-1 (0.5 ML injected)	DAF C-2 (1ML injected)	DAF C-3 (2ML injected)
0.5	1,798	903	454
1	5,238	2,620	1,314
1.5	9,700	4,850	2,425
2	15,015	7,500	3,758
3	27,600	13,800	6,900

5.6.2. Further uses of the DAF values

When a site-specific assessment has to be undertaken, the DAF values can be used to derive predicted environmental concentrations (PEC) for specific receptors provided an estimate of the chemical concentration at the source (the coal seams affected by the stimulation activity) is available. The PEC values would be obtained by dividing the source concentration by the relevant DAF values (see Table 5-27 for some hypothetical examples). Such PECs can subsequently be used to inform human health and/or environmental risk assessments (NICNAS 2017a).

Another potential use is the derivation of maximum chemical concentrations of hydraulic fracturing fluids for safe operations: based on the DAF values, maximum chemical concentrations at the well site (based on an individual well or on a series of wells if risks of cumulative effects are plausible) can be derived that would not lead to exceeding the no-effect concentration for given receptors. This would provide a metric that can be monitored and thus managed at the well site. Alternatively, it may be used to derive a limit to the total injected chemical mass at a well field to ensure the maximum chemical concentrations for safe operations are not exceeded (see Figure 5-30 for some examples; injected volumes are total hydraulic fracture volume).

In addition, DAF values could also be used to derive limits for safe half-life ($T_{1/2}$) values, to further limit potential impacts on receptors (see example in Figure 5-31). Indeed, if substances with similar chemical action are available, then preference could be given to those that have demonstrated degradation potential under anaerobic conditions and with acceptable half-life. Table 5-27 Selection of hydraulic fracturing chemicals with previously estimated concentrations prior to injection – CPI (NICNAS 2017c). Calculated predicted environmental concentrations (PEC) for 1ML of injected fluids at three travel distances from injection source. $\#Na_2CO_3$ - Alternative names: sodium carbonate, soda ash: when dissolved in water, it forms carbonic acid (H_2CO_3) and sodium hydroxide (NaOH). @NaClO – althernative names: sodium hypochlorite, chloride of soda, bleach: when dissolved in water, it forms chlorine and sodium hydroxide.

CAS No.	CAS Chemical Name	Conc. After Final Dilution Prior to Injection (mg/kg or mg/L)	PEC at 1 km (mg/L)	PEC at 2 km (mg/L)	PEC at 3 km (mg/L)
10043-35-3	Boric acid (H ₃ BO ₃)	216	8.24E-05	2.88E-05	1.57E-05
107-21-1	1,2-Ethanediol	496	1.89E-04	6.61E-05	3.59E-05
1310-73-2	Sodium hydroxide (Na(OH))	137.5	5.25E-05	1.83E-05	9.96E-06
26172-55-4	3(2H)-Isothiazolone, 5-chloro-2- methyl-	3.7	1.41E-06	4.93E-07	2.68E-07
2682-20-4	3(2H)-Isothiazolone, 2-methyl-	1.1	4.20E-07	1.47E-07	7.97E-08
497-19-8	Carbonic acid sodium salt (1:2)#	2,532,000	9.66E-01	3.38E-01	1.83E-01
55566-30-8	Phosphonium, tetrakis(hydroxymethyl)-, sulfate (2:1) (salt)	41.25	1.57E-05	5.50E-06	2.99E-06
64-19-7	Acetic acid	525	2.00E-04	7.00E-05	3.80E-05
67-63-0	2-Propanol	13.4	5.11E-06	1.79E-06	9.71E-07
7447-40-7	Potassium chloride (KCl)	22,963	8.76E-03	3.06E-03	1.66E-03
75-57-0	Methanaminium, N,N,N-trimethyl-, chloride (1:1)	1,273	4.86E-04	1.70E-04	9.23E-05
7647-01-0	Hydrochloric acid	52.5	2.00E-05	7.00E-06	3.80E-06
7681-52-9	Hypochlorous acid, sodium salt (1:1)@	57.7500	2.20E-05	7.70E-06	4.18E-06
7727-54-0	Peroxydisulfuric acid ([(HO)S(O) ₂]2O ₂), ammonium salt (1:2)	452.1	1.73E-04	6.03E-05	3.28E-05
7786-30-3	Magnesium chloride (MgCl ₂)	3.4	1.30E-06	4.53E-07	2.46E-07
77-92-9	1,2,3-Propanetricarboxylic acid, 2- hydroxy-	1,765	6.74E-04	2.35E-04	1.28E-04
9000-30-0	Guar gum	2,600	9.92E-04	3.47E-04	1.88E-04
111-76-2	2-butoxyethanol	40	1.53E-05	5.33E-06	2.90E-06
7647-14-5	Sodium chloride	400	1.53E-04	5.33E-05	2.90E-05



Figure 5-30 Estimated maximum chemical concentration prior to injection for different injection volumes (total hydraulic fracture volume in ML, megalitres) and distances to the nearest receptor (0.5, 1, and 2 km). Based on DAF values from Table 5-26 (dispersion/dilution only) and PNEC values from Table 5-24. Higher permissible concentrations may be obtained if degradation can be demonstrated.



Figure 5-31 Estimated maximum half-life T_{1/2} (days) to achieve a given DAF for three travel distances to the nearest receptor (0.5, 1, and 2 km) (based on dilution/dispersion model C-2, without sorption).

5.6.3. Usage of methodology and DAF values outside study areas

The methodology, including the use of the DAF tool, can be used in any other region if pathways are characterised in terms of i) travel time and travel time classes and ii) attenuation potential that can be expected along the particle pathways. This requires that i) particle tracking analysis is undertaken to characterise travel time distributions, and ii) the hydrogeology is sufficiently characterised (broad mineralogy and hydrochemistry) to derive geological and chemical (for organics and radionuclides) attenuation factors. In other words, the hazard screening methodology has a broad applicability; however, applicability of the specific DAF values derived in this study to other regions requires careful consideration of pathways, travel times and attenuation potential.

The applicability of current DAF values elsewhere can be addressed by considering the three broad groups of processes that contribute to attenuation:

- Flow-related attenuation owing to dilution and dispersion (high applicability): DAF values derived for this type of attenuation are valid for both organic and inorganic chemicals. DAF values based on the relatively short travel distances and injected volumes discussed in Section 5.6.1 and related uses of DAF values (Sections 5.6.2 and 5.6.3) have a high applicability elsewhere. The main reason being that dilution and dispersion within coal target formations within relatively short distances from the chemical source (up to 2-3 km) are likely similar to very similar across most sedimentary coal basins. In some cases applying dilution factors based on dilution and dispersion only might be enough to reduce concentrations to a low risk level and further analysis involving dilution attenuation factors due to sorption and/or degradation might not be required. Practically, the recommended use of current DAF values (owing to dilution and dispersion) is as part of a screening step in chemical risk and/or environmental impact assesments.
- Geological attenuation due to sorption onto organic carbon and minerals (medium to low applicability): DAF values based on geological attenuation (sorption of organics and inorganics) make use of site-specific information on sorption characteristics of geological media (including organic carbon, mainly in the coal seams). Other information such as formation water hydrochemistry (pH, dissolved compounds such as carbonates) may be equally important in determining sorption behaviour. In basins where geological media and formation hydrochemistry are similar to the conditions of this study, applicability of current DAF values would be medium.

In this case, its recommended use is restricted to being part of a screening step in chemical risk and/or environmental impact assessments. Where such conditions are markedly different, applicability would be low and requires reassessing DAF values based on the current methodology, also for screening purposes.

Chemical or biological attenuation as a result of degradation (organics) or decay (radionuclides) (medium applicability): In addition to dilution due to dilution/dispersion and sorption, organic compounds (and radionuclides) will be subject to further dilution owing to chemical or biological degradation. Formation hydrochemistry, including redox potential (aerobic or anaerobic), and presence of microbial communities that facilitate biological degradation are key conditions that determine potential for this type of attenuation. For basins with similar conditions as those considered in this study, applicability of current DAF values would be medium. In this case, its recommended use is restricted to being part of a screening step in chemical risk and/or environmental impact assesments. If such conditions are considerably different, applicability would be low and requires reassessing DAF values based on the current methodology, also for screening purposes.

Particle tracking analyses require a calibrated groundwater flow model with sufficient spatial discretisation to represent the CSG well fields and have a reasonable spatial granularity in representing the potentially impacted receptors. The software requirements for undertaking particle tracking analysis are straightforward, with tested simulators such as MODPATH, which is a free-domain particle-tracking post-processing model that computes three-dimensional flow paths using output from groundwater flow simulations based on MODFLOW (Harbaugh 2005). The program uses a semianalytical particle-tracking scheme that allows an analytical expression of a particle's flow path to be obtained within each finite-difference grid cell. These are very CPU efficient calculations that require only a fraction of the time needed to run the groundwater flow model. Particle tracking calculations do not require additional data, except for the locations (X, Y, Z) of the receptor and contaminant source.

Specifically, the applicability of the DAF values for the Bandanna Formation (Bowen Basin, QLD) is discussed next. The Surat Basin is underlain by the Bowen Basin, with the Clematis/Showground Sandstones as major aquifers and the Bandanna Formation as the main target formation (OGIA 2016). These aquifers are separated from the above Precipice Sandstone by the Moolayember Formation (aquitard) and from the underlying Bandanna Formation by the Rewan Group (aquitard) (Table 2-25). The Bandana Formation is mainly composed of sandstone, siltstone, mudstone, carbonaceous mudstone, coal and oil shale. This is similar to the Walloon Coal Measures, which is mainly composes of fine to medium-grained lithic sandstone, siltstone, mudstone, and coal (OGIA 2016).

Consistent with the general discussion on applicability of DAF values (see above), the applicability of current DAF values will be discussed on the basis of the three broad groups of processes that contribute to attenuation:

- Flow-related attenuation owing to dilution and dispersion: Median permeability in the Bandanna Formation is 0.17 22 mD; by comparison, median permeability for the Walloon Coal Measures (Surat Basin) is from 0.12 mD to 35 mD (OGIA 2016). Coal porosity of Walloon Coal Measures is 1% (OGIA 2016); although no reliable porosity data are available for the Bandanna Formation, it is not expected to be significantly larger owing to its greater burial depth. Given the similarity in permeability and inferred similarity in porosity, it is expected that when the same volume of hydraulic fracturing fluid is injected, similar chemical plumes will develop in the coal seams and interburden. Therefore, hydraulic fracturing into the Bandanna coal formations is not expected to yield significantly less dilution and dispersion than in the Walloon Coal Measures. DAF values based on dilution and dispersion are therefore applicable to the Bandanna Formation.
- Geological attenuation due to sorption onto organic carbon and minerals:
 - Sorption onto organic carbon: The thickness of the Bandanna Formation can be more than 500 m but is generally between 150 and 200 m. Coal seam thickness within the Bandanna Formation is variable and can reach up to 10 m, but averages less than 2 m (OGIA 2016). Santos (2014) reported coal seam thicknesses between 8-9 m with 6 coal seams across a 60 100 m thick Bandanna Formation. Based on the latter data, the scaling factor for organic carbon is therefore between 0.48 (48/100) and 0.9 (54/60). This is higher than for the Walloon Coal Measures, where average total formation thickness was 375 m and coal seam thickness 15 m, yielding a scaling factor of 15/375 = 0.04. As a result, the

available carbon for sorption of organic chemicals introduced into the Bandanna Formation coal seams does not appear to be less than for the Walloon Coal Measures. Therefore, the opportunity for sorption and thus geological attenuation is not expected to be less than for the Walloon Coal Measures (discussed in Section 4.3.3.1.2). DAF values for organic chemicals are thus considered applicable to the Bandanna Formation.

- Sorption onto minerals: Based on the similarity in lithology (sandstone/siltstone/mudstone/coal), pH (7.8 for Bandanna compared to 8 for Walloon Coal Measures, TDS (2,500 mg/L for Bandanna compared to 1,700 3,800 mg/L for Walloon Coal Measures), and redoxpotential (both assumed to be anaerobic), the sorption potential for norganic chemicals is considered similar to that for the Walloon Coal Measures (for hydrochemistry data for Bandanna Formation, see OGIA 2016). DAF values for inorganic chemicals are considered applicable to the Bandanna Formation.
- Chemical or biological attenuation as a result of degradation (organics) or decay (radionuclides): Based on similarities in hydrochemistry and redox potential (assumed anaerobic), the potential for chemical (hydrolysis) and/or anaerobic biological attenuation is assumed similar. DAF values for organic chemicals derived under conditions of anaerobic degradation or hydrolysis are considered applicable to the Bandanna Formation.

5.6.4. Key assumptions that underpin analyses and results

Key assumptions that underpin the current analyses and results are as follows:

- The results of the study are predicated on current scientific understands in several different fields, including geology, hydrogeology, groundwater modelling, toxicology and ecotoxicology, and fracture modelling techniques. Similarly, the results are heavily informed by current or near-current groundwater models used in Queensland and New South Wales. Significant changes to the underlying scientific paradigms or groundwater models, as new information emerges, may warrant reconsideration of these results.
- 2. The study further assumes vertical CSG wells; a single CSG well per well pad; one hydraulic fracture operation per well over the life of the well; and every well in the case study area is hydraulically fractured.
- 3. The study also assumes a relatively constant well spacing (approximately 1 well/ km²), especially in undertaking the solute particle tracking simulations.
- 4. No faults or faulting was considered in the groundwater flow models that were the basis for the solute particle tracking; while this assumption is valid for the considered case study areas, a different approach may need to be invoked when flow paths are modified by the presence of fault zones, whether they act as conduits or barriers to flow (McCallum et al. 2016).
- 5. Chemical half-lives for CSG chemicals considered here will be similar to those reported in this study.
- 6. Most / all receptors are connected to relatively small recharge areas, and that at most a couple of CSG wells per receptor could contribute to accumulation effects.
- 7. Chemical hazards can effectively be assessed individually, i.e. there are no significant additive or synergistic mixture toxicity effects.

6. Research outcomes and outputs

6.1. **Research outcomes**

Specific outcomes from this assessment include:

- rigorous, independent, and transparent science that significantly strengthens the level of knowledge about potential groundwater contamination from CSG chemicals in Australia, and what risks they may pose to the public and the environment,
- this knowledge base directly informs our understanding of which chemicals can continue to be used safely, and which chemicals are likely to require extra monitoring, industry management and regulatory consideration,
- improved evidentiary base to inform regulatory and CSG industry decision making regarding the planning, operation and monitoring of CSG well fields,
- research addressing a major IESC research priority and known knowledge gap, resulting in new scientific information being available to the IESC and others when developing advice for regulatory decision makers,
- improved community confidence in i) safety of hydraulic fracturing operations in regards to potential risks to deeper groundwater, ii) regulatory decision making regarding the risks from hydraulic fracturing chemicals used in CSG extraction in Australia.

6.2. **Research outputs**

Regarding potential sources of organic and inorganic contaminants, the outputs of this research include:

- published information on the suite of chemicals used in hydraulic fracturing fluids,
- data on organic and inorganic geogenic contaminants (identity, toxicity, concentrations, and time dependency of concentrations) in coal seam waters,
- better understanding of the risk for large-scale migration of geogenic organic and inorganic contaminants that may have been mobilised through interactions between coal and hydraulic fracturing fluids;
- determination of degradation/transpormation pathways and parameters quantifying the potential for organic chemicals to break down in the water phase for use in solute transport models; sorption/desorption behaviour of hydraulic fracturing chemicals for use in solute transport models.

Regarding pathways for contaminant migration:

- better understanding of the risks posed by leaky wells (due to well rupture during injection),
- assessment of likelihood and characteristics of fracture growth into a well through pre-fracturing permeability and new fractures,
- assessment of likelihood and characteristics of fracture growth into aquifers, and fracture growth into a fault,
- set of conceptual models (pictorials) to help communicate the issues and provide a common basis for informed discussions.

Regarding receptor-pathway analysis:

- potential economic, ecological, and sociocultural receptors identified, including a spatial analysis of their proximity to CSG wells, resulting in proximity-likelihood functions for two test case areas (Gunnedah Basin and Surat Basin),
- for a limited number of plausible pathways, undertake solute particle-tracking analysis to explore the degree of isolation of the target coal seam formations from other groundwater systems with previously identified receptors; established travel time and travel distance statistics for use in analysis of attenuation and overall risk

Regarding attenuation capacity of the deeper groundwater:

- better understanding of the attenuation capacity of the subsurface (dilution/dispersion, sorption, degradation/transformation) for coal seam gas chemicals,
- derivation of dilution attenuation factors for key hydrostratigraphic units in the Gunnedah and Surat basin that integrate effects of all relevant attenuation processes,
- derivation of setback distances that ensure sufficient attenuation to reduce CSG chemical concentrations in the deeper groundwater to safe levels.

6.3. Has this research improved the existing evidence base?

By means of improved process understanding for all components of the source-pathway-receptor chain we have significantly improved the evidence base available to those assessing potential risks posed to deeper groundwater from chemicals used in drilling and hydraulic fracturing. Improvement of the evidence base for each component is as follows:

- Does a contaminant source exist in deeper groundwater? By identifying chemicals that have previously been
 rigorously assessed and found to be of low concern to the environment and/or human health dentify, a highthroughput screening provides evidence to determine for which chemical a contaminant source exists in deeper
 groundwater. If a chemical is not 'of low concern', the evidence base for that chemical is expanded to include its
 attenuation behaviour in the coal seam formations following hydraulic fracturing, its mobility, and spatial extent of
 contaminant plume. This will inform whether or not there is a conceivable risk for contamination (e.g. if bounding
 estimates demonstrate that the potential for dilution and attenuation is very high, no further more detailed pathway
 analysis would be required).
- What happens along the identified pathways? For a number of plausible fate and transport release pathways, contaminant fate has been generically quantified including effects of attenuation as a natural means to decrease concentrations. This will provide insight into timescales of migration, residual concentrations at receptor endpoints, and potential cumulative effects along the pathway (e.g. mass accumulation by aggregation of pathways).
- What is the potential exposure for humans and the environment? By providing robust estimates of predicted concentrations in groundwater, consequences for humans and the environment will be assessed more reliably. By linking the consequences (i.e. degree of attenuation) with likelihood for such attenuation to occur, the overall likelihood for low or high exposure levels to chemicals can be determined.

Who benefits from the results?

- Communities: improved understanding of CSG extraction processes and its risks, leading to a better acceptance of CSG industry, and increased trust in CSG industry; a better management of industry practices will result in reduced risk to human health; additional revenue stream for landholders and communities,
- Government and regulators: strengthened (i.e. science-based) regulatory regime, reduced uncertainty about potential impacts and thus more confidence in approving or rejecting new projects, independent peer-reviewed reference material available for government and regulator

• Industry: better underpinning of social licence to operate, more effective fracturing operations with less risk for failure, better management of risks associated with CSG extraction, less uncertain regulatory regime, secure access to sufficient amounts of locally produced gas to meet demands.

7. Summary

A two-level hazard screening framework was developed and tested which involved, at Level 1, a cost-effective highthroughput screening of CSG chemicals that have previously been rigorously assessed and found to be of low concern to the environment and/or human health (that is, "of low concern"), and for chemicals not screened out at Level 1 a further analysis, Level 2, to allow ranking and evaluation of the chemical hazard on the basis of a calculated dilution attenuation factor (DAF).

The site-independent Level 1 screening used existing lists and rules for screening chemicals and lists of chemicals that have previously been rigorously assessed and found to be of low concern to the environment and/or human health ("of low concern"). This involved consideration of data on health effects and ecotoxicity and the intrinsic physico-chemical properties of the chemical that will affect potential exposure.

The Level-2 analysis combined:

- spatial analyses of contaminant source-receptor proximities (shortest distance between CSG wells and receptors identified within the asset registers developed within the Bioregional Assessment Program) resulting in proximity-frequency relationships for different groups of receptors,
- chemical/biological, geological (due to sorption) and flow-related (dilution/dispersion) attenuation information for a selection of characteristic chemicals,
- the conceptual models with plausible fate and transport release pathways and calculation tools required to estimate the degree of attenuation that chemicals would experience prior to potentially reaching receptors.

Mainly to inform and strengthen the Level-2 analysis, a national and international literature review was undertaken with a focus on plausible pathways for hydraulic fracturing fluids to migrate from the gas well to a groundwater resource, hazard screening approaches, chemical toxicity, and exposure assessment methodologies. Several studies in the USA concluded that hydraulic fracturing itself appears not to present a significant environmental risk, except when abandoned or suspended well casings are intersected by fracturing fluids during the high-pressure stage of fluid injection. Geomechanical modelling and experimental studies generally agree that physical constraints on hydraulic fracture propagation will, in the USA, prevent induced fractures from extending from deep zones into drinking water resources. This is in contrast to the Australian contexts, where stock and domestic bores already screen into the target coal measures. Several studies highlighted that maintaining good well integrity is the key to minimising many of the risks associated with hydraulic fracturing and unconventional resource extraction. Likewise, producing gas wells situated in the same target formation as new gas wells involved with fracture stimulation may be affected by hydraulic fracturing fluids when the inter-wellbore distance is less than approximately 250 m.

To demonstrate the Level-2 analysis, representative chemicals have been selected for assessment of attenuation and dilution from typical chemical groups (chemical indicators) that represent different behaviour in regards to:

- physicochemical properties mobility (geological attenuation) and persistence (biological and chemical attenuation),
- health effects and ecotoxicity,
- chemical use for CSG extraction in Australia.

The chemicals tested include typical hydraulic fracturing and drilling chemicals (*acrylamide polymer, boron* (*boric acid, borax*), *bronopol, limonene, methyl-chloro-isothiazolinone*), explosives used to obtain a pattern of perforations through the casing and cement sheath (HMX: *cyclotetramethylene trinitramine*), and several geogenic chemicals (*2-methylphenol, naphthalene, uranium, arsenic*, and *barium*).

Building on the literature review on plausible fate pathways, the following four plausible fate and transport release scenarios have been developed for which the chemical-specific DAF in groundwater-related receptors have been assessed:

- Fracture growth into an overlying aquifer (Pathway A): This scenario considers hydraulic fracture fluid loss into an overlying aquifer. The scenario considers site conditions that favour height growth of a vertical hydraulic fracture upward towards and into a shallower aquifer.
- Fracture growth into a well through pre-fracturing permeability and new fractures (Pathway B): This involves two wells within the same coal seam, connected by a pre-existing hydraulic facture.
- Well rupture during injection (Pathway C): This scenario considers rupture of a cased well during a fracturing injection operation.
- Fracture growth into a fault (Pathway D): assessment of leakage potential via a fault that connects the coal seam to an overlying aquifer.

By applying multiple lines of quantitative and semi-quantitative evidence and expert judgements to each plausible pathway, the assessment concluded that pathways are either unlikely (high to very high confidence for Pathway C) or extremely unlikely (<5% probability for Pathways A, B, and D) in an Australian context.

A spatial analysis of proximity of ecologic, economic and socio-cultural assets to CSG wells in subdomains of the Gunnedah and Surat Basins provided insight in the number and frequency of such assets that were at close distance from existing or planned CSG wells. Cumulative probability plots of distance of assets from CSG wells illustrate CSG wells are generally at large to very large distances from the above three classes of assets. For instance, the probability of encountering a CSG well within 1 km distance from an asset ranges from about 1% (assets in the Groundwater Dependent Ecosystems Class) to 0.02 % (water bores in the Gunnedah Basin Water Access Right class). In the Surat Basin a similarly small fraction of assets was encountered within 1 km of CSG wells, i.e. 0.3% for assets within the Groundwater Dependent Ecosystems class and 0.4% for water bores (Water Access Right class). Surface water features at a distance of 1 km from CSG wells had probabilities of 2% in the Gunnedah Basin while in the Surat Basin there was no surface water feature within 29 km of a CSG well. No sociocultural asset was within less than 13 km from the nearest CSG well in the Gunnedah Basin and less than 40 km in the Surat Basin.

In a subsequent analysis, solute particle tracking analysis with existing regional-scale groundwater models was undertaken to identify if the previously identified assets could potentially be connected to CSG well locations through groundwater in the unlikely event that plausible fate pathways existed (Pathways A-D). In the subdomains of the Gunnedah and Surat Basins where particle tracking was undertaken, the number of potential connections was found to be relatively small. Where connections had been identified, the travel time through groundwater was determined to be very long, from hundreds to tens of thousands of years. The reason for these long timescales is the combination of large separation distances, slow groundwater velocities and the presence of low permeability formations effectively isolating receptors at the surface from deeper groundwater pathways. For the same assets, the proximity to the connected wells was also determined as a means to assign a likelihood to the degree of solute attenuation associated with a given pathway.

From the literature study, a baseline set of chemical degradation constants (half-lives) and sorption coefficients were derived. These values where then rescaled to specific geological formations within the two case study areas, taking into account the fraction of organic carbon with each formation. On the basis of rescaled degradation constants (half-lives), chemical (hydrolysis) and microbiological degradation (aerobic or anaerobic) was calculated for a series of organic compounds that are either present in hydraulic fracturing fluid or that occur naturally in coal formations. Calculations considered conservative travel distances that were encountered in the particle tracking analysis. Particle tracking analysis resulted in several travel time groups (0-100 years, 100-1000 years, etc.). The first travel time group of up to 100 years yielded minimum, mean, and maximum travel times of 10, 34, and 92 years, respectively; these travel times were selected for the calculation of chemical mass loss in deeper groundwater following hydraulic fracturing. The calculation considered first only degradation without sorption. In a second calculation degradation was combined with sorption. In a third calculation a three-dimensional advection-dispersion analytical solution model was invoked to determine dilution and dispersion as the third process of attenuation. Dilution attenuation factors (DAF) were derived for the different travel

times and the combined attenuation processes. For the shortest (10 years), mean (34 years), and maximum (92 years) travel time considered, the DAF were all extremely large (from nearly 1,000 to more than 10¹⁰) owing to the combined effect of short half-lives, sorption (for those hydrostratigraphic units where organic carbon is present), and dilution/dispersion over travel distances from 0.5 to 3.4 km.

In a final analysis, the calculated DAF values were linked to the frequency-proximity results: in this way a likelihood was assigned to DAF values indicating that small DAF values (short travel times) have a very low likelihood in the areas investigated.

A relationship was derived between the minimal chemical travel distance or setback distance that is required to achieve a given DAF value based on known predicted-no-effect-concentrations (PNEC) and chemical concentrations prior to injection. The setback distance is the conservative minimal distance between a CSG well and a receptor that is considered sufficient to reduce the chemical concentration to values below regulatory limits or no-effect levels. The most conservative setback distance does not account for additional attenuation due to sorption and/or degradation. Less conservative setback distances can be obtained if also attenuation due to degradation and sorption is accounted for. Based on the broad range of types of organic and inorganic hydraulic fracturing and geogenic chemicals evaluated, a setback distance of 2 km would satisfy the DAF criteria for most of the chemicals considered in this study.

Based on consideration of the eleven chemicals (drilling chemicals, hydraulic fracturing chemicals, and geogenic chemicals), the overall conclusions from this study are formulated as follows:

- If the risk is measured at receptors such as those in the Bioregional Assessment register (including groundwater dependent ecosystems at or near the land surface), then this study indicates that the risk for contamination of deeper groundwater by coal sea gas chemicals is small to very small for the two case study areas and for the eleven chemicals involved at the Level-2 analysis. This conclusion has a very high level of confidence.
- If the risk is assessed at receptors such as "groundwater" the methods described here can be used to calculate an 'offset distance' from hydraulically fractured CSG wells beyond which risks are low. For example, assuming a fracking fluid volume of 1 ML and concentrations set out in Table 5-23, the point of assessment must be at least 500 m (2-butoxyethanol, naphthalene, arsenic, barium, boron, uranium), or 2,000 m for methyl-chloro-isothiazolinone (MCI), from the CSG well to ensure that concentrations will fall below the predicted no effect concentrations (PNEC) for the protection of aquatic freshwater biota and drinking water guideline concentrations for Australia (for naphthalene a recommended maximum drinking water concentration from the US was used). This conclusion has a very high level of confidence.
- It was not possible to extend this example at receptors such as "groundwater" for 2-methylphenol, limonene, HMX, bronopol, and acrylamide polymer cannot at present be determined with a very high level of confidence due to lack of data on concentrations prior to injection and/or PNEC and drinking water guide values for these chemicals. However, based on the derived DAF for each of these chemicals, the required point of assessment relative to a CSG well to ensure small to very small risks is very likely similar to those of the chemicals for which sufficient data for assessment was available. This conclusion has a high level of confidence.

Evidence to underpin these conclusions include:

- An assessment of the likelihood of each of four plausible fate and transport release pathways, with the conclusion being that such pathways are either unlikely (with a high to very high confidence) or extremely unlikely (<5% probability) in an Australian context,
- A spatial analysis of proximity of ecologic, economic and sociocultural assets to CSG wells in subdomains of the Gunnedah and Surat Basins, which showed that the majority were at large (km) to very large (tens of km) distance from existing or planned CSG wells,
- A numerical particle tracking analysis using state-of-the-art regional-scale groundwater models, demonstrating in the subdomains of the Gunnedah and Surat Basins where particle tracking was undertaken, that the number of potential connections between CSG well locations and existing receptors was found to be relatively small. Where

connections had been identified, the travel time through groundwater was determined to be very long, from hundreds to tens of thousands of years,

- Calculations of attenuation potential for organic compounds on the basis of degradation constants (half-lives)
 obtained from the literature, which indicated that for the long travel times typical of the two case study areas,
 chemical (hydrolysis) and microbiological (aerobic or anaerobic) degradation processes together with sorption
 onto organic matter would easily reduce chemical concentrations to below any hazardous level,
- Calculations of attenuation potential due to dilution and dispersion, which provided another line of evidence that, for the large travel distances, a significant decrease in chemical concentration can be obtained (also for inorganic chemicals).
- A comparison of the concentration of hydraulic fracturing chemicals prior to injection with PNEC values for chronic and overall aquatic ecotoxicity, which illustrated that the required attenuation to yield concentrations in groundwater that are not harmful is easily obtained by the dilution processes considered for a distance between CSG well and receptor of approximately 2 km. The same conclusion was reached when a comparison was made between the maximum concentrations of inorganic elements measured in laboratory tests (where coal samples were subjected to acidic fluids to simulate effects of hydraulic fracturing fluids on release of inorganic elements) and their water quality guidelines for aquatic ecosystem protection.

Recommendations for further research include:

- The attenuation calculations could be extended to the transformation products by using the degradation pathways identified herein this report. This requires further data collection regarding half-lives and sorption behaviour for each of the transformation products. These calculations might help confirm that none of the transformation products could bioaccumulative because of a long half-life,
- The list of chemicals with available PNEC data for ecosystem protection could be expanded such that minimal DAF values to achieve levels 'of low concern' could be derived (provided their chemical concentration prior to injection is known). The same holds true for chemicals without drinking water guideline values,
- Evaluation of mixture toxicity. This could include determination of the necessary input parameters needed to develop a concentration additive model such as toxicitiy units for each contaminant and characterisation of the modes of toxic interaction.
- Qualification of predictive uncertainty. A more systematic analysis of predictive uncertainty is warranted to
 capture are key sources of uncertainty such that reliable confidence intervals can be defined for particular
 outputs, such as the DAF values. Being able to apportion overall uncertainty to various contributing processes,
 parameters and boundary or initial conditions will allow future investments to be more targeted and aimed at
 reducing only those uncertainties that are key contributors to the overall uncertainty. This would be especially
 valuable with regards to particle tracking analysis, as the current calculations are based on relatively coarse flow
 models with limited resolution in the hydrogeological models.

8. References

- Abraham WR, Hoffmann HMR, Kieslich K, Reng G, and Stumpf B (1985). Microbial transformation of some monoterpenoids and sesquiterpenoids. Ciba Foundation symposium, III: 146–160.
- Abrams D, Haitjema H, and Kauffman L (2013). On modeling weak sinks in MODPATH. Groundwater 51: 597–602.
- Adey J (2005). Development of the partition coefficient (Kd) test method for use in environmental risk assessments. UK Environment Agency Science Report SC020039/4, 67 pages.
- Ahamad PYA, Kunhi AAM, and Divakar S (2001). New metabolic pathway for o-cresol degradation by Pseudomonas sp. CP4 as evidenced by 1H NMR spectroscopic studies. World Journal of Microbiology and Biotechnology 17: 371-377.
- Allen DT, Torres VM, Thomas J, Sullivan DW, Harrison M, Hendler A, Herndon SC, Kolb CE, Fraser MP, Hill AD, Lamb BK, Miskimins J, Sawyer RF, and Seinfeld JH (2013). Measurements of methane emissions at natural gas production sites in the United States. Proceedings of the National Academy of Science 110: 18023–18024.
- Ames LL, McGarrah JE, and Walker BA (1983). Sorption of trace constituents from aqueous solutions onto secondary minerals. 1. Uranium. Clays and Clay Minerals 31: 321-334.
- Anderman ER and Hill MC (2001). MODFLOW-2000, The U.S. Geological Survey Modular Ground-Water Model -Documentation of the Advective-transport observation (ADV2) Package, Version 2: U.S. Geological Survey Open-File Report 01-54, 69 p.
- ANZECC/ARMCANZ (2000). Australian and New Zealand guidelines for fresh and marine water quality. National Water Quality Management Strategy, Document 4. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- APLNG (2015). 2014-2015 Groundwater assessment report (Q-1000-75-RP-001). 436 pp.
- APPEA (2014). Chemicals and compounds used in CSG Fraccing Factsheet. APPEA (Australian Petroleum Production and Exploration Association). Available from www.appea.com.au/wp-content/uploads/2014/08/CSG-fraccing-chemicals.pdf
- APPEA (2015). Additional data and information provided by industry to Office of Water Science (Department of Environment) as part of The National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia. APPEA (Australian Petroleum Production and Exploration Association).
- Appelo CAJ and Postma D (2004). Geochemistry, groundwater and pollution. Second Edition. AA Balkema Publishers, Leiden, The Netherlands.
- Apte SC, Williams M, Kookana RS, Batley GE, King JJ, Jarolimek CV, and Jung RF (2017a). Release of geogenic contaminants from Australian coal seams: experimental studies, Project report, report prepared by the Land and Water Flagship, Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Apte SC, Williams M, Kookana RS, Batley GE, King JJ, Jarolimek CV, and Jung RF (2017b). Literature review of geogenic contaminants associated with the hydraulic fracturing of coal seams. Project report, report prepared by the Land and Water Flagship, Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Aronson D, Printup H, Shuler K, and Howard P (1998). Chemical Fate Half-Lives for Toxics Release Inventory (TRI) Chemicals. Syracuse Research Corporation. Environmental Science Center SRC TR 98-008.
- ATSDR (1997). Toxicological Profile of HMX. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- ATSDR (1998). Toxicological Profile for 2-butoxyethanol and 2-butoxyethanol acetate. U.S Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- ATSDR (2005). Public Health Statement: Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- ATSDR (2007a). Toxicological Profile for Barium and Barium Compounds. PBS2008-100003. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- ATSDR (2007b). Toxicological Profile for Arsenic. Agency for Toxic Substances and Disease Registry. PB2008-100002, August 2007. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- ATSDR (2008). Toxicological Profile for Cresols. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- Aziz CE, Newell CJ, Gonzales JR, Haas P, Clement TP, Sun Y-W (2000). BIOCHLOR Version 1.0 User's Manual. EPA/600/R-00/008.
- Aziz CE, Newell CJ, and Gonzales JR (2002). BIOCHLOR. Natural attenuation decision support system. Air Force Center for Environmental Excellence Technology Transfer Division.
- Bagi A, Pampanin DM, Brakstad OG, and Kommedeal R (2013). Estimation of hydrocarbon biodegradation rates in marine environments: A critical review of the Q10 approach. Marine Environmental Research 89: 83-90.
- Bagi A, Pampanin DM, Lanzen A, Brakstad OG, and Kommedeal R (2014). Naphthalene biodegradation in temperate and arctic marine microcosms. Biodegradation 25: 111-125.
- Bair ES, Freeman DC, and Senko JM (2010). Subsurface gas invasion, Bainbridge Township, Geauga County, Ohio: Expert Panel Technical Report: Submitted to Ohio Dept. of Natural Resources, Division of Mineral Resources Management: accessed April 18, 2016, http://www.dnr.state.oh.us/bainbridge/tabid/20484/Default.aspx.
- Balakrishnan VK, Halasz A and Hawari J (2003). Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX, and CL-20: New insights into degradation pathways obtained by the observation of novel intermediates. Environmental Science and Technology 37(9): 1838-1843.
- Batley GE, van Dam R, Warne MSJ, Chapman JC, Fox DR, Hickey CW and Stauber JL (2014). Technical rationale for changes to the method for deriving Australian and New Zealand water quality guideline values for toxicants. CSIRO Land and Water Report, 37 pp.
- Beatson RK and Newsam GN (1992). Fast evaluation of radial basis functions. Computers and Mathematics with Applications 24(12): 7-19.
- Binet MT, Batley G, Hickey C, Golding LA and Adams MS (2016). Guidelines for the protection of aquatic ecosystems, toxicant trigger values: Boron – Freshwater. Australian and New Zealand guidelines for fresh and marine water quality. Draft July 2016. Council of Australian Governments Standing Council on Environment and Water, Canberra, ACT, Australia.
- Boethling RS and Sabljic A (1989). Screening-level model for aerobic biodegradability based on a survey of expert knowledge. Environmental Science and Technology 23:672-679.
- Boethling RS, Howard PH, Meylan W, Stiteler W, Beaumann J, Tirado N (1994). Group contribution method for predicting probability and rate of aerobic biodegradation. Environmental Science and Technology 28:459-465.
- Boronina A, Renard P, Balderer W, and Stichler W (2005). Application of tritium in precipitation and in groundwater of the Kouris catchment (Cyprus) for description of the regional groundwater flow. Applied Geochemistry 20: 1292–1308. doi:10.1016/j.apgeochem.2005.03.007.
- Bowen HJM (1966). Trace elements in biochemistry, New York, Academic Press, p. 19.
- Boyd SA, Johnston CT, Laird DA, Teppen BJ, and Li H (2011). Comprehensive study of organic contaminant adsorption by clays: methodologies, mechanisms, and environmental implications. In Biophysico-Chemical Processes of Anthropogenic Organic Compounds in Environmental Systems 51-71, John Wiley & Sons, Inc., Hoboken, NJ, USA.
- Boyd SA (1982). Adsorption of substituted phenols by soils. Soil Science 134(5): 337-343.
- Brannon JM, Price CB, Yost SL, Hayes C, and Porter B (2005). Comparison of environmental fate and transport process descriptors of explosives in saline and freshwater systems. Marine Pollution Bulletin 50(3): 247-251.

- Brantley SL, Yoxtheimer D, Arjmand S, Grieve P, Vidic R, Pollak J, Llewellyn GT, Abad J, and Simon C (2014). Water resource impacts during unconventional shale gas development: The Pennsylvania experience. International Journal of Coal Geology 126: 140-156.
- Broermann J, Bassett RL, Weeks EP, and Borgstrom M (1997). Estimation of αL, velocity, Kd and confidence limits from tracer injection test data. Ground Water 5: 1066–1076.
- Broomfield M (2012). Support to the identification of potential risks for the environment and human health arising from hydrocarbons operations involving hydraulic fracturing in Europe. Report for European Commission DG Environment, (17), 1–192. http://doi.org/AEA/R/ED57281.
- Bunger AP (2015). Introduction to Hydraulic Fracturing Mechanics and Applications. University of Pittsburgh.
- Bunger AP, Kear J, Lecampion B, and Quesada D (2010). The geometry of a hydraulic fracture growing along a wellbore annulus. 9th HSTAM Int. Con. on Mechanics. Limassol, Cyprus, 12-14 July 2010. pp 341-350.
- Byrne RH and Laurie SH (1999). Influence of pressure on chemical equilibria in aqueous systems with particular reference to seawater. Pure and Applied Chemistry 71: 871-890.
- Campin D (2015). Environmental Regulation of Hydraulic Fracturing. Society of Petroleum Engineers Operations and Productions: 1-33.
- Carbajo JB, Perdigón-Melón JA, Petre AL, Rosal R, Letón P, and García-Calvo E (2015). Personal care product preservatives: Risk assessment and mixture toxicities with an industrial wastewater. Water Research 72: 174-185.
- Caulfield MJ, Qiao GG, and Solomon DH (2002). Some aspects of the properties and degradation of polyacrylamides. Chemical Reviews 102(9): 3067-3083.
- CCME (1991). Boron. Guidelines for Canadian Drinking Water Quality, Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment, http://healthycanadians.gc.ca/publications/healthy-living-viesaine/water-boron-bore-eau/alt/water-boron-bore-eau-eng.pdf (accessed 20 June 2016)
- CCME (1999a). Canadian water quality guidelines for the protection of aquatic life: Phenols Mono- and dihydric phenols. In: Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, Winnipeg, 5 pages.
- CCME (1999b). Canadian Water Quality Guidelines for the Protection of Aquatic Life; Polycyclic aromatic hydrocarbons (PAHs). In: Canadian Environmental Quality Guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CCME (2009). Scientific criteria document for the development of the Canadian Water Quality Guidelines for boron. Canadian Council of Ministers of the Environment. Report No. PN1437, Ottawa, Canada, 63 pp.
- CCME (2011). Canadian Water Quality Guidelines for the Protection of Aquatic Life; Uranium. In: Canadian Environmental Quality Guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CDM Smith (2014). Santos Narrabri Gas Project Groundwater Impact Assessment, Subiaco, Western Australia.
- Cerniglia CE (1984.) Microbial metabolism of polycyclic aromatic hydrocarbons. Advances in Applied Microbiology 30: 31-71.
- Challis BC and Yousaf TI (1990). Facile formation of N-nitrosamines from bromonitromethane and secondary amines. Journal of the Chemical Society, Chemical Communications. 22: 1598–1599.
- Commonwealth of Australia (2004). Approved Criteria for Classifying Hazardous Substances, 3rd edition, National Occupational Health and Safety Commission (NOHSC) NOHSC: 1008 (2004), Safe Work Australia.
- Commonwealth of Australia (2014a). Background review: Bore integrity. Department of the Environment, Canberra.
- Commonwealth of Australia (2014b). Background review: Hydraulic fracturing ('fraccing') techniques, including reporting requirements and governance arrangements. Department of the Environment, Canberra.
- COT (2006). COT Statement on uranium levels in water used to reconstitute infant formula. UK Committee of Chemicals in Food, Consumer Products and the Environment, COT statement 2006/07, May 2006.
- Council of Canadian Academies (2014). Environmental Impacts of Shale Gas Extraction in Canada.

- Covello VT (1983). The perception of technological risks: A literature review. Technological Forecasting and Social Change 23(4): 285-297.
- Covello VT (1992). Risk Communication: An Emerging Area of Health Communication Research. In S. A. Deetz (Ed.), Communications Yearbook. Newbury Park (CA): Sage Publications.
- CTFA (1992). Final report on safety assessment of methylisothiazolinone and methylchloroisothiazolinone. Journal of the American College of Toxicology 11:75-127.
- Cui N, Zhang X, Xie Q, Want S, Chen J, Huang L, Qiao X, Li X, and Cai X (2011). Toxicity profile of labile preservative bronopol in water: The role of more persistent and toxic transformation products. Environmental Pollution 159: 609-615.
- Davies RJ, Mathias SA, Moss J, Hustoft S, and Newport L (2012). Hydraulic fractures: How far can they go? Marine and Petroleum Geology 37: 1-6. http://dx.doi.org/10.1016/j.marpetgeo.2012.04.001
- Day S, Dell'Amico M, Fry R, and Tousi HJ (2014). Field Measurements of Fugitive Emissions from Equipment and Well Casings in Australian Coal Seam Gas Production Facilities: Report to the Department of the Environment. CSIRO Report.
- de Maagd PG-J, ten Hulscher DThEM, van den Heuvel H, Opperhuizen A, and Sijm DTHM (1998). Physicochemical properties of polycyclic aromatic hydrocarbons: Aqueous solubilities, n-octanol/water partition coefficients, and Henry's law constants. Environmental Toxicology and Chemistry 17:251–257.
- Department of Mines and Petroleum (2013). Environmental Risk Assessment of Chemicals used in WA Petroleum Activities Guideline.
- DNRM (2011). Loss of well control. Petroleum and gas safety alert no. 48, 22 June 2011, Version 1. Department of Natural Resources and Mines.
- DNRM (2013). Code of practice for constructing and abandoning coal seam gas wells and associated bores in Queensland. Department of Natural Resources and Mines. Edition 2.0.
- DNRM (2015). Surat Basin Groundwater Chemistry Baseline Assessment Database. Supplied by OGIA (Department of Natural Resources and Mines).
- Doble R, McCallum J, Turnadge C, Peeters L, Wu B, Mallants D (2016). Modelling inter-aquifer leakage associated with well integrity failure, prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Canberra.
- DoEE (2016a). Draft National Standard: National Standard for Environmental Risk Management of Industrial Chemicals. Report prepared by GHD for the Department of the Environment and Energy, November 2016, 31/33665. Commonwealth of Australia, Canberra.
- DoEE (2016b). National Standard for Environmental Risk Management of Industrial Chemicals: Discussion Paper. Report prepared by GHD for the Department of the Environment, March 2016, 31/33665. Commonwealth of Australia, Canberra.
- DoEE (2017a). Literature review: Environmental risks from coal seam gas operations, report prepared by the Chemicals and Biotechnology Assessments Section (CBAS) of the Department of the Environment and Energy as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- DoEE (2017b). Environmental risk assessment framework for the coal seam gas industry risk assessment, report prepared by the Chemicals and Biotechnology Assessments Section (CBAS) of the Department of the Environment and Energy as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Denome SA, Stanley DC, Olson ES, and Young KD (1993). Metabolism of dibenzothiophene and naphthalene in Pseudomonas Strains: Complete DNA sequence of an upper naphthalene catabolic pathway. Journal of Bacteriology 175: 6890-6901.
- Dhavalikar RS and Bhattacharayya PK (1966). Microbial transformation of terpenes: Part VIII Fermentation of limonene by a soil pseudomonad. Indian Journal of Biochemistry 3:144–157.

- Dixit S and Hering JG (2003). Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environmental Science and Technology 37: 4182–4189.
- Douglass ML, Kabacoff BL, Anderson GA, and Chent MC (1978). The chemistry of nitrosamine formation, inhibition and destruction. Journal of the Society of Cosmetics Chemistry 29: 581–606.
- Domenico PA (1987). An analytical model for multidimensional transport of a decaying contaminant species. Journal of hydrology 91: 49-58.
- Domenico PA and Robbins GA (1986). A new method of contaminant plume analysis. Groundwater 24(4): 476-485.
- DOW (1993). The glycol ethers handbook. DOW Chemical Co. Midland MI.
- DPandE (2014). Coal seam gas exclusion zones. Retrieved 5 August, 2016, from <u>http://www.planning.nsw.gov.au/coal-seam-gas-exclusion-zones</u>.
- Duetz WA, Fjallman AHM, Ren S, Jourdat C, and Witholt B (2001). Biotransformation of D-Limonene to (1) trans-Carveol by Toluene-Grown Rhodococcus opacus PWD4 Cells. Applied and Environmental Microbiology 67: 2829–2832.
- Dunnett PC and Telling GM (1984). Study of the fate of bronopol and the effects of antioxidants on N-nitrosamine formation in shampoos and skin creams. International Journal of Cosmetic Science 6 (5): 241–247. DOI: 10.1111/j.1467-2494.1984.tb00381.x.
- Dusseault M and Jackson R (2014). Seepage pathways assessment for natural gas to shallow groundwater during well stimulation, in production, and after abandonment. Environmental Geosciences 21(3): 107–126, doi:10.1306/eq.04231414004.
- Dyer S (2001). Determination of the aquatic PNEC (0.05) for boron. Chemosphere 44: 369-376.
- Eastern Star Gas (2008). Dewhurst-2 well completion report. PEL-238, Gunnedah Basin, NSW.
- EC (2003). Naphthalene Summary risk assessment report. European Commission Special Publication I.03.81.17 pp.
- EFSA (2008). European Food Safety Authority. Scientific Opinion of the Panel on Plant Protection Products and their Residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. The EFSA Journal (2007) 622, 1-32. http://www.efsa.europa.eu/sites/default/files/scientific_output/files/main_documents/622.pdf
- Engelder T (2012). Capillary tension and imbibition sequester frack fluid in Marcellus gas shale. Proceedings of the National Academy of Sciences USA, 10.1073/pnas.1216133110.
- Engelder T, Cathless LM, and Bryndzia LT (2014). The fate of residual treatment water in gas shale. Journal of Unconventional Oil and Gas Resources 7: 33-48.
- enHealth Human Risk Assessment (HHRA) (2012). Environmental Health Risk Assessment, Guidelines for Assessing Human Health Risks from Environmental Hazards. Office of Health Protection of the Australian Government Department of Health.
- Environment Canada (2003). Guidance Manual for the Categorisation of Organic and Inorganic Substances on Canada's Domestic Substances List. Determining Persistence, Bioaccumulation Potential and Inherent Toxicity to Non-Human Organisms, Existing Substances Branch, Environment Canada, June 2003. <Available on request from Environment Canada at ESB.DSE@ec.gc.ca>.
- EPHC (2009a). Environmental Risk Assessment Guidance Manual for Industrial Chemicals. Prepared by Australian Environment Agency Pty Ltd for DoE, formerly Environment Protection Branch Department of the Environment, Water, Heritage and the Arts. Environment Protection and Heritage Council, available at <http://www.scew.gov.au/resource/chemical-risk-assessment-guidance-manuals>.
- EPHC (2009b). Environmental Risk Assessment Guidance Manual: for agricultural and veterinary chemicals. Environment Protection and Heritage Council (EPHC). Commonwealth of Australia, Canberra.
- Erdal BR, Aguilar RD, Bayhurst BP, Daniels WR, Duffy CJ, Lawrence FO, Maestas S, Oliver PQ, and Wolfsberg K (1979). Sorption-desorption studies on granite. I. Initial studies of strontium, technetium, cesium, barium, cerium, europium, uranium, plutonium, and americium. LA-7456-MS Informal Report.

- Esterle JS, Hamilton SK, Ward V, Tyson S, and Sliwa R (2013). Scales of Geological Heterogeneity within the Walloon Subgroup and its Coal Measures. February 2013. Final report of Activity 1.3 of the Healthy Head Waters Coal Seam Gas Water Feasibility Study. Department of Natural Resources and Mines.
- European Union (1998). Council Directive 98/83/EC on the quality of water intended for human consumption. Official Journal of the European Communities. L330.
- Fetter CW (1993). Contaminant hydrogeology. Macmillan Publishing Company. 458 pages.
- Fisher M and Warpinski N (2012). Hydraulic fracture height growth: Real data. Society of Petroleum Engineers Production and Operations 27: 8-19. http://dx.doi.org/10.2118/145949-PA.
- Flewelling SA, Tymchak MP, and Warpinski N (2013). Hydraulic fracture height limits and fault interactions in tight oil and gas formations. Geophysical Research Letters 40: 3602-3606. http://dx.doi.org/10.1002/grl.50707
- Fort DJ, Propst TL, Stover EL, Murray FJ, and Strong PL (1999). Adverse effects from low dietary and environmental boron exposure on reproduction, development and maturation in Xenopus laevis. Journal of Trace Elements in Experimental Medicine 12: 175-185.
- GasFields Commission Queensland (2015). Onshore Gas Well Integrity in Queensland, Australia. Technical Communication 4 July 2015.
- Gassiat C, Gleeson T, Lefebvre R, and McKenzie J (2013). Hydraulic fracturing in faulted sedimentary basins: Numerical simulation of potential contamination of shallow aquifers over long time scales. Water Resources Research 49: 8310–8327, doi:10.1002/2013WR014287.
- GHD (2012). Surat Cumulative Management Area Groundwater Model Report. Report for QWC17-10 Stage 2. Queensland Water Commission.
- Gopalakrishan S, McKellar J, Fitzell M, and Troup A (2015). Hylogger™: A new tool for mineralogical correlation of stratigraphy. Geological Survey of Queensland, Department of Natural Resources and Mines.
- Government of Canada (2000). Persistence and Bioaccumulation Regulations, SOR/2000-107.
- Goyal AK and Zylstra GJ (1997). Genetics of naphthalene and phenanthrene degradation by Comamonas testosteroni. Journal of Indian Microbiology and Biotechnology 19: 401-407.
- Grigorescu M (2011). Mineralogy of the north-eastern Bowen Basin and north-eastern Surat Basin, Queensland (CD ROM). Geological Survey of Queensland - Record 2011/02 22pp.
- Guiton S, Kieft R, Churchill J, and Sheerin C (2015). Characterising the Hutton Sandstone in the Northeastern Surat Basin. AAPG Asia Pacific Region, Geoscience Technology Workshop, Opportunities in Coal Bed Methane in the Asia Pacific, Brisbane.
- Gusyev MA, Abrams D, Toews MW, Morgenstern U, and Stewart MK (2014). A comparison of particle-tracking and solute transport methods for simulation of tritium concentrations and groundwater transit times in river water. Hydrology and Earth System Sciences 18: 3109–3119.
- Guyonnet D and Nevill C (2007). Dimensionless analysis of two analytical solutions for 3-D solute transport in groundwater. Journal of Contaminant Hydrology 75: 141-153.
- Haderlein SB and Schwarzenbach RP (1993). Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces. Environmental Science and Technology 27(2): 316-326. DOI: 10.1021/es00039a012.
- Hale SE, Endo S, Arp HPH, Zimmerman AR, and Cornelissen G (2015). Sorption of the monoterpenes α -pinene and limonene to carbonaceous geosorbents including biochar. Chemosphere 119: 881-888.
- Haley M, McCawley M, Epstein AC, Arrington B, and Bjerke EF (2016). Adequacy of current state setbacks for directional high-volume hydraulic fracturing in the Marcellus, Barnett, and Niobrara Shale plays. Environmental Health Perspectives February 2016.
- Halliburton Fluids Disclosure.

http://www.halliburton.com/public/projects/pubsdata/hydraulic_fracturing/fluids_disclosure.html; accessed May 2016

- Hansen B (2011). Casing perforating overview. Devon Energy Corporation Proceedings of the technical workshops for the hydraulic fracturing study: well construction and operations, EPA 600/R-11/046, May 2011.
- Harbaugh AW (2005). MODFLOW-2005: the U.S. Geological Survey modular ground-water model the ground-water flow process. Book 6: Modeling techniques, Section A. Ground-water.
- Harris O, Wilbur S, George J, and Eisenmann C (1998). Toxicological profile for 2-Butoxyethanol and 2-Butoxyethanol acetate. US Department of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry.
- Harris JC (1990). Rate of hydrolysis. In: Lyman WJ, Rheehl WF, Rosenblatt DH, eds. Handbook of Chemical Property Estimation Methods. Washington, DC: American Chemical Society, 7-4.
- Hawari J, Beaudet S, Halasz A, Thiboutot S, and Ampleman G (2000). Microbial degradation of explosives: biotransformation versus mineralization. Applied Microbiology and Biotechnology 54: 605-618.
- Hawari J, Halasz A, Beaudet S, Paquet L, Ampleman G, and Thiboutot S (2001). Biotransformation routes of Octahydro-1,3,5,7-tetranitro-1,3,5,7- tetrazocine by Municipal Anaerobic Sludge. Environmental Science and Technology 35: 70-75.
- Health Canada (2001). Guidelines for Canadian Drinking Water Quality: Supporting Documentation. Uranium. Health Canada, Ottawa, Ontario, Canada.
- Health Canada (2006). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document for Arsenic. Health Canada, Ottawa, Ontario, Canada.
- Health Canada (2008). Guidelines for Canadian Drinking Water Quality Summary Table, p.14. Federal-Provincial-Territorial Committee on Drinking Water, Federal-Provincial-Territorial Committee on Health and the Environment.
- Health Canada (2010). Tetrakis (hydroxymethyl) phosphonium sulfate. Evaluation Report ERC2010-02. Pest Management Regulation Agency, Health Canada, Ottawa, Canada.
- Helfferich F (1962). Ion exchange. McGraw-Hill Book Co., New York.
- Helsel DR and Hirsch RM (2002). Statistical Methods in Water Resources. Techniques of Water-Resources Investigations of the United States Geological Survey, Book 4, Hydrologic Analysis and Interpretation, Chapter A3, U.S. Geological Survery.
- Henderson B, Hayes KR, O'Grady A, Mount R, Lewis S, Schmidt RK, Dambacher J, Barry S, Holland K and Raiber M (2015).
 Developing the conceptual model of causal pathways. Submethodology M05 from the Bioregional Assessment
 Technical Programme. Department of the Environment, Bureau of Meteorology, CSIRO and Geoscience Australia,
 Australia (in preparation). Viewed 23 March 2017, http://data.bioregionalassessments.gov.au/submethodology/
 M05.
- Heys KA, Shore RF, Pereira MG, Jones KC and Martin FL (2016). Risk assessment of environmental mixture effects. RSC Advances 6: 47844-47857.
- Herbes SE and Schwall LR (1978). Microbial Transformation of Polycyclic Aromatic Hydrocarbons in Pristine and Petroleum-Contaminated Sediments. Applied and Environmental Microbiology 35: 306-316.
- Horowitz A, Shelton DR, Cornell CP, and Tiedje JM (1982). Anaerobic degradation of aromatic compounds in sediments and digested-sludge. Developments in Industrial Microbiology 23: 435-444.
- Howard PH (1989). Naphthalene. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Jarvis, W. F., G.W. Sage, D.K. Basu, D.A. Gray, W. Meylan, E.K. Crosbie, E. K., Eds. Lewis Publishers: Chelsea, MI. Vol. 1: 408-422.
- Howard PH, Boethling RS, Jarvis WF, Meylan WM, and Michalenko EM (1991). Handbook of Environmental Degradation Rates. Lewis, Chelsea, MI, USA.
- Hughes MF, Beck BD, Chen Y, Lewis AS, and Thomas DJ (2011). Arsenic exposure and toxicology: A historical perspective. Toxicological Sciences 123: 305–332.
- Hunt B (1983). Mathematical Analysis of Groundwater Resources. Butterworth & Co., London. 271 pp.
- Hurst A, Scott A, and Vigorito M (2011). Physical characteristics of sand injectites. Earth Science Reviews 106: 215-246.

- Huyakorn PS, Ungs MJ, Mulkey LA, and Sudicky EA (1987). A three-dimensional analytical model for predicting leachate migration. Groundwater 25(5): 588-598.
- Huysmans M and Dassargues A (2005). Review of the use of Peclet numbers to determine the relative importance of advection and diffusion in low permeability environments. Hydrogeology Journal 13: 898-904.
- IAEA (2001). Environmental Isotopes in the Hydrological Cycle: Principles and Applications, vol. 1. International Atomic Enegy Agency and UNESCO, Vienna.
- IARC (2004). Arsenic in drinking water. International Agency for Research on Cancer.
- IOM (2001). Dietary reference intakes for Vitamin A, Vitamin K, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc. Institute of Medicine, National Academy Press, Washington, DC.
- IPCS (2001a). Barium and barium compounds. Concise International Chemical Assessment Document 33. International Programme on Chemical Safety, World Health Organisation, Geneva, Switzerland.
- IPCS (2001b). Environmental Health Criteria 224: Arsenic and arsenic compounds. International Programme on Chemical Safety, World Health Organisation, Geneva, Switzerland.
- Jacobson A and Williams TM (2000). The environmental fate of isothiazolone biocides. Chimica Oggi 18(10): 105-108.
- Jackson RB, Vengosh A, Darrah TH, Warner NR, Down A, Poreda RJ, Osborn SG, Zhao K, and Karr JD (2013). Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. Proceedings of the National Academy of Sciences 110: 11250-11255. http://dx.doi.org/10.1073/pnas.1221635110.
- Jackson RB (2014). The integrity of oil and gas wells. Proceedings of the National Academy of Sciences: 2. www.pnas.org/cgi/doi/10.1073/pnas.1410786111.
- Janardhanan S and Moore C (2015). CSG Water Injection Impacts: Modelling, Uncertainty and Risk Analysis Groundwater flow and transport modelling and uncertainty analysis to quantify the water quantity and quality impacts of a coal seam gas produced water injection scheme in the Surat Basin, Queensland. CSIRO, Australia: 96 pp.
- Jaoui M, Achard C and Rogalski M (2002). Solubility as a function of temperature of selected chlorophenols in aqueous solutions containing electrolytes or surfactants. Journal of Chemical and Engineering Data 47: 297-303.
- Jaramillo AM, Douglas TA, Walsh ME, and Trainor TP (2011). Dissolution and sorption of hexahydro-1,3,5-trinitro-1,3,5triazine (RDX) and 2,4,6-trinitrotoluene (TNT) residues from detonated mineral surfaces. Chemosphere 84(8): 1058-1065.
- Jeffrey R, Zhang X, Chen Z, Wu B, Kear J, and Kasperczyk D (2017a). Simulation of loss of fluid from a hydraulic fracture into an aquifer, report prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Jeffrey R, Zhang X, Chen Z, Wu B, Kear J, and Kasperczyk D (2017b). Literature review for coal seam gas hydraulic fracture growth and well integrity, report prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Johnson Jr L, Flottman T, and Campagna DJ (2002). Improving Results of Coalbed Methane Development Strategies by Integrating Geomechanics and Hydraulic Fracturing Technologies, SPE paper 77824 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition held in Melbourne, Australia, 8-10 Oct 2002.
- Johnson RL, Scott MP, Jeffrey RG, Chen ZR, Bennett L, Vendenborn C, and Tcherkashnev S (2010). Evaluating Hydraulic Fracture Effectiveness in a Coal Seam Gas Reservoir from Surface Tiltmeter and Microseismic Monitoring, In: Society of Petroleum Engineers Annual Technical. Society of Petroleum Engineers, Florence, Italy.
- Kahrilas GA, Blotevogel J, Stewart PS, and Borch T (2014). Biocides in Hydraulic Fracturing Fluids: A Critical Review of Their Usage, Mobility, Degradation, and Toxicity. Environmental Science and Technology 49: 16-32.
- Kear J, White J, Bunger AP, Jeffrey R, and Hessami M-A (2013). Three Dimensional Forms of Closely-Spaced Hydraulic Fractures. Effective and Sustainable Hydraulic Fracturing 693–707. http://doi.org/http://dx.doi.org/10.5772/56261.

- King G (2012). Hydraulic Fracturing 101: What Every Representative, Environmentalist, Regulator, Reporter, Investor, University Researcher, Neighbor and Engineer Should Know. Society of Petroleum Engineers Hydraulic Fracturing Technology Conference, 1–80. Retrieved from <u>http://www.onepetro.org/mslib/servlet/onepetropreview?id=SPE-152596-MS</u>.
- King GE and King DE (2013). Environmental Risk Arising From Well Construction Failure: Differences Between Barrier Failure and Well Failure and Estimates of Failure Frequency Across Common. SPE Annual Technical Conference and Exhibition, (October), Society of Petroleum Engineers–166142–MS. http://doi.org/10.2118/166142-MS.
- Kim J and Moridis GJ (2013). Development of the T1M coupled flow–geomechanical simulator to describe fracture propagation and coupled flow–thermal–geomechanical processes in tight/shale gas systems. Computers and Geosciences 60: 184–198.
- Kissinger A, Helmig R, Ebigbo A, Class H, Lange T, Sauter M, Heitfeld M, Klunker J, and Jahnke W (2013). Hydraulic fracturing in unconventional gas reservoirs: Risks in the geological system, part 2. Environmental Earth Sciences 70(8): 3855–3873, doi:10.1007/s12665-013-2578-6.
- Kiyohara H, Torigoe S, Kaida N, Asaki T, Iida T, Hayashi H, and Takizawa N (1994). Cloning and characterization of a chromosomal gene cluster, pah, that encodes the upper pathway for phenanthrene and naphthalene utilization by Pseudomonas putida OUS82. Journal of Bacteriology 176: 2439-2443.
- Kollig HP (1993). Environmental Fate Constants for Organic Chemicals Under Consideration for EPA's Hazardous Waste Identification Projects. EPA Report EPA/600/R-93/132, Environmental Research Lab., U.S. EPA, Athens, GA.
- Kopinke FD, Porschmann J, and Stottmeister U (1995). Sorption of organic pollutants on anthropogenic humic matter. Environmental Science and Technology 29: 941-950.
- Kühn R and Pattard M (1990). Results of the harmful effects of water pollutants to green algae (Scenedesmus subspicatus) in the cell multiplication inhibition test. Water Resources 24: 31–38.
- Kühn R, Pattard M, Pernak K-D, and Winter A (1989). Results of the harmful effects of water pollutants to *Daphnia Magna* in the 21 day reproduction test. Water Research 23(4): 501-510.
- Langmuir D (1978). Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica Acta 42: 547–569.
- Lenda A and Zuber A (1970). Tracer dispersion in groundwater experiments. Proceedings of a Symposium on the Use of Isotopes in Hydrology. IAEA, Vienna, pp. 619–641. March 9–13.
- Leij F and Bradford SA (1994). 3DADE: A computer program for evaluation of three-dimensional equilibrium solute transport in porous media. Research Report No. 134, US Salinity Lab, Riverside, CA.
- Lewin U, Wennrich L, Efer J, and Engewald W (1997). Determination of highly polar compounds in water samples around former ammunition plants. Chromatographia 45: 91-98.
- Lewis J, Martel R, Trepanier L, Ampleman G, and Thiboutot S (2009). Quantifying the transport of energetic materials in unsaturated sediments from cracked unexploded ordonance. Journal of Environmental Quality 38: 2229-2236.
- Linge H (1989). The surface area of coal particles. Fuel 68 (1): 111-113.
- Lintott D and Tindal M (2007). Estimation of a generic adsorption coefficient Kd for barium. Report for the British Columbia upstream petroleum environmental task group, barite-barium issues subgroup, 19 pages.
- Loehr RC (1989). Treatability potential for EPA listed hazardous wastes in soil. Environmental Research Laboratory, Office of Research and Development, United States Environmental Protection Agency. Ada, Oklahoma.
- Loeppky RN (1994). Nitrosamine and N-Nitroso Compound Chemistry and Biochemistry. ACS Symposium Series, American Chemical Society: Washington, DC, USA.
- Loewengart G (2001). Toxicity of boron to rainbow trout: a weight-of-the-evidence assessment. Environmental Toxicology and Chemistry 20: 796-803.
- Lyman WJ Reehl WF, and Rosenblatt DH (1990). Handbook of Chemical Property Estimation Methods. Washington, DC: American Chemical Society, Washington DC 960 pp.

- Madsen T, Buchardt Boyd H, Nylén D, Pedersen AR, Petersen GI, and Simonsen F (2001). Environmental and Health Assessment of Substances in Household Detergents and Cosmetic Detergent Products. Environmental Project No. 615.
- Mahajan O (1984). Physical characterization of coal. Powder Technology 40 (1-3): 1-15.
- Malik M. and Letey J (1991). Adsorption of polyacrylamide and polysaccharide polymers on soil materials. Soil Science Society of America Journal 55(2): 380-383.
- Mallants D, Dierckx A, Wang L, and Volckaert H (2001). Impact assessment analysis for surface storage of radioactive waste addressing radiotoxicity and chemotoxicity: Application to an existing radium-waste surface storage facility. Proceedings of the 8th International Conference on Radioactive Waste Management and Environmental Remediation, ICEM01, Brugge October 1- 4, 2001.
- Mallants D, Raiber M, and Davies P (2016). Decision Support System for investigating gas in water bores and links to coal seam gas development. Report prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) for the Queensland Department of Natural Resources and Mines, Australia.
- Mallants D, Bekele E, Schmid W, and Miotlinski K (2017a). Human and environmental exposure conceptualisation for soil to shallow groundwater pathways, Project report, report prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Mallants D, Bekele E, Schmid W, Miotlinski K, and Bristow K CSIRO (2017b). Literature review: Leakage to shallow groundwater of fluids associated with hydraulic fracturing for coal seam gas extraction, Project report, report prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- Marquis RE and Matsumura P (1978). Microbial life under pressure. Chapter 4 in Microbial Life in Extreme Environments, Kushner, D. Ed. Academic Press, London, 464 pages.
- Martin-Hayden JM and Robbins GA (1997). Plume Distortion and Apparent Attenuation Due to Concentration Averaging in Monitolring Wells. Groundwater 35 (2): 339-346.
- Mastrandrea MD, Field CB, Stocker TF, Edenhofer O, Ebi KL, Frame DJ, Held H, Kriegler E, Mach KJ, Matschoss PR, Plattner G-K, Yohe GW, and Zwiers FW (2010). Guidance Note for Lead Authors of the IPCC Fifth Assessment Report on Consistent Treatment of Uncertainties. Intergovernmental Panel on Climate Change (IPCC). Available at http://www.ipcc.ch.
- Mayo-Bean K, Moran K, Meylan B, and Ranslow P (2012). Methodology document for the ECOlogical Structure-Activity Relationship Model (ECOSAR) Class Program. Estimating toxicity of industrial chemicals to aquatic organisms using the ECOlogical Structure-Activity Relationship class program. MS-Windows Version 1.11 Office of Pollution Prevention and Toxics U.S. Environmental Protection Agency 1200 Pennsylvania Ave., N.W. Washington, DC.
- Maxwell SC (2011). Hydraulic Fracture Height Growth. CSEG Recorder, (November), 18-22.
- Mazurek, M, Alt-Epping, P, Bath, A, Gimmi, T, Waber, HN, Buschaert, S, De Canniere, P, De Craen, M, Gautschi, A, Savoye, S, Vinsot, A, Wemeare, I, Wouters, L (2011). Natural tracer profiles across argillaceous formations. Applied Geochemistry 173: 219-240.
- McCallum J, Simmons C, Mallants D and Batelaan O (2016). Simulating the groundwater flow dynamics of fault zones. MODFLOW Un-Structured Grid: A comparison of methods for representing fault properties and a regional implementation. Report to the Office of Water Science, Department of the Environment, Canberra. Prepared by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Canberra.
- McGuire KJ and McDonnell JJ (2006). A review and evaluation of catchment transit time modelling. Journal of Hydrology 330: 543–563. doi:10.1016/j.jhydrol.2006.04.020.
- Meylan WM and Howard P (1995). Atom/Fragment Contribution Method for Estimating Octanol-Water Partition Coefficients. Journal of Pharmacological Sciences 84: 83-92.
- Michaux M, Nelson E, and Vidick B (1989). Cement chemistry and additives. Oilfield review 1(1): 18-25.

Mihelcic JR and Luthy RG (1988). Degradation of polycyclic aromatic hydrocarbon compounds under various redox conditions in soil-water systems. Applied and Environmental Microbiology 54(5): 1182-1187.

- Mikami Y (1988). Microbial conversion of terpenoids. Biotechnology and genetic engineering reviews (6): 271-320.
- Mitchell P, Bruce J, O'Grady A, Read A, and Holland KL (2015). Description of the receptor register for the Maranoa-Balonne-Condamine subregion. Product 1.4 for the Maranoa-Balonne-Condamine subregion from the Northern Inland Catchments Bioregional Assessment. Department of the Environment, Bureau of Meteorology, CSIRO and Geoscience Australia, Australia. http://data.bioregionalassessments.gov.au/product/NIC/MBC/1.4.
- MITI (1992). Biodegradation and bioaccumulation data of existing chemicals based on the CSCL Japan compiled under the supervision of Chemical Products Safety Division, Basic Industries Bureau, Ministry of International Trade and Industry, Japan. Ministry of International Trade and Industry, Chemicals Inspection and Testing Institute (ISBN 4-89074-101-1).
- MoH NZ (2008). New Zealand Ministry of Health, Drinking-water standards for New Zealand 2005 (Revised 2008), p. 175, Ministry of Health, Wellington.
- Monteil-Rivera F, Groom C, and Hawari J (2003). Sorption and degradation of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in soil. Environmental Science and Technology 37(17): 3878-3884.
- Mueller DT and Eid RN (2006). Characterization of early-time mechanical behavior of well cements employed in-surface casing operations: IAD/SPE Drilling Conference, Miami, Florida, IADC/SPE 98632, 11 p.
- Muller G (1981). Thermal stability of high-molecular-weight polyacrylamide aqueous solutions. Polymer Bulletin 5(1): 31-37.
- Muller G, Fenyo JC, and Selegny E (1980). High molecular weight hydrolysed polyacrylamids 3. Effect of temperature on chemical stability. Journal of Applied Polymer Science 25(4): 627-633.
- Muuri E (2015). The sorption and diffusion of 133Ba in granitic rocks. Master's Thesis University of Helsinki.
- Myers T (2012). Potential Contaminant Pathways from Hydraulically Fractured Shale to Aquifers. Groundwater 50(6): 872-882.
- Navi M, Skelly C, Taulis M, and Nasiri S (2015). Coal seam gas water: potential hazards and exposure pathways in Queensland. International Journal of Environmental Health Research 25(2): 162-183.
- NHMRC and NHMMC (2011). Australian Drinking Water Guidelines 2011. National Water Quality Management Strategy, Document 6, Version 3.3, updated November 2016. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.
- NICNAS (2013). NICNAS Handbook—a guide for importers and manufacturers of industrial chemicals in Australia, accessed in May 2016, http://www.nicnas.gov.au/regulation-and-compliance/nicnas-handbook.
- NICNAS (2015). Identification of chemicals of low concern to human health, Inventory Multi-tiered Assessment and Prioritisation Framework, National Industrial Chemicals Notification and Assessment Scheme, accessed July 2016, http://www.nicnas.gov.au/chemical-information/imap-assessments/the-imap-framework.
- NICNAS (2017a). Human health and environmental risks associated with surface spills and leaks of chemicals, Project report, report prepared by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- NICNAS (2017b). Chemicals of low concern for human health, Project report, report prepared by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.
- NICNAS (2017c). Identification of chemicals associated with coal seam gas extraction in Australia, Project report prepared by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) as part of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia, Commonwealth of Australia, Canberra.

- NRMMC (2011). Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.
- NSW Petroleum (onshore) Act (1991). Petroleum (Onshore) Act 1991 No 84, 78 pp.
- NSW Office of Water (2011). Characterisation of hydrochemistry and risks to groundwater quality. Impact of groundwater pumping on groundwater quality: National Water Commission Raising National Water Standards Programme.
- NSW Chief Scientist and Engineer (2012). Draft letter from Chief Scientist and Engineer to Minister Hartcher on the likelihood of hydraulic fracturing activities in NSW.
- NSW Chief Scientist and Engineer (2014a). Final report on the independent review of coal seam gas activities in NSW, September 2014.
- NSW Chief Scientist and Engineer (2014b). Independent review of coal seam gas activities in NSW, Information paper: fracture stimulation activities, September 2014.
- NSW Chief Scientist and Engineer (2014c). Independent review of coal seam gas activities in NSW, Information paper: abandoned wells, September 2014.
- NSW Chief Scientist and Engineer (2014d). Independent Review of Coal Seam Gas Activities in NSW Information paper: On managing the interface between coal seam gas activities and other land uses (Setbacks), September 2014.
- NUDLC (2012). Minimum construction requirements for water bores in Australia, Third Edition. National Uniform Drillers Licensing Committee. ISBN 978-0-646-56917-8.
- Ochs M, Mallants D, and Wang L (2015). Radionuclide and metal sorption on cement and concrete. Topics in Safety, Risk, Reliability and Quality. Volume 29. Springer International Publishing Switzerland 2015, ISBN 978-3-319-23650-6, DOI 10.1007/978-3-319-23651-3301 pp. 301.
- OECD (1981). OECD guidelines for testing of chemicals. Organisation for Economic Co-operation and Development, Paris.
- OECD (2014). The OECD Environmental Risk Assessment Toolkit: Tools for Environmental Risk Assessment and Management. Organisation for Economic Co-operation and Development, Paris.
- OEHHA (2003). Public Health Goal for Barium in Drinking Water. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.
- OGIA (2016). Underground Water Impact Report for the Surat Cumulative Management Area. Office of Groundwater Impact Assessment, Department of Natural Resources and Mines, Queensland.
- O'Grady AP, McNamara J, Welsh WD, Holland KL, Aryal SK, Mount RE, and Marston FM (2015). Description of the waterdependent asset register for the Namoi subregion. Product 1.3 for the Namoi subregion from the Northern Inland Catchments Bioregional Assessment. Department of the Environment, Bureau of Meteorology, CSIRO and Geoscience Australia, Australia.
- Orem WH, Tatu C, Lerch HE, Rice CA, Bartos TT, Bates AL, Tewalt S, and Corum MD (2007). Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA. Applied Geochemistry 22:2240-2256.
- Orem W, Tatu C, Varonka M, Lerch H, Bates A, Engle M, Crosby L, and McIntosh J (2014). Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. International Journal of Coal Geology 126: 20–31.
- Park KS, Sims RC, Dupont RR, Doucette W, and Matthews JE (1990). Fate of PAH compounds in two soil types: Influence of volatilization, abiotic loss and biological activity. Environmental Chemistry 9: 187-195.
- Papendick SL, Downs KR, Vo KD, Hamilton SK, Dawson GKW, Golding SD, and Gilcrease PC (2011). Biogenic methane potential for Surat Basin, Queensland coal seams. International Journal of Coal Geology 88, 123–134.
- Parliament of New South Wales (2011). Coal seam gas exploration, by Buckingham The Hon Jeremy, Hansard 10 August 2011.
- Pennington JC and Brannon JM (2002). Environmental fate of explosives. Thermochimica Acta 384(1-2): 163-172.

- Piatt JJ, Backhus DA, Capel PD, and Eisenreich SJ (1996). Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments. Environmental Science and Technology 30: 751-760.
- Podoll RT, Irwin KC, and Parish HJ (1989). Dynamic studies of naphthalene sorption on soil from aqueous solution. Chemosphere 18(11-12): 2399-2412.
- Pollock D (2012). User Guide for MODPATH Version 6—A Particle-Tracking Model for MODFLOW. Chapter 41 of Section A, Groundwater Book 6, Modeling Techniques and Methods 6–A41.
- Price KS, Waggy GT, and Conway RA (1974). Brine shrimp bioassay and seawater BOD of petrochemicals. Journal of the Water Polution Control Federation 46 (1):63-77.
- Prommer H, Rathi B, Donn M, Siade A, Wendling L, Martens E, and Patterson B (2016). Geochemical response to reinjection. Final Report. CSIRO, Australia.
- QGC (2012). Approval conditions 49 to 52: Stage 2 CSG Water Monitoring and Management Plan. 2nd Revision to 23 April 2012 submission. 13.0 Well stimulation.
- Queensland Government (2014). Queensland Legislation: Bills introduced to the 53rd Parliament. Retrieved August 5, 2016, from https://www.legislation.qld.gov.au/Bill_Pages/Bill_53_11.htm.
- QWC (2012). Underground water impact report for the Surat Cumulative Management Area. Queensland Water Commission. 224 pp.
- Ransley T, Sommerville P, Piang Tan K, Feitz A, Cook S, Yates G, Schoning G, Bell J, Caruana L, Sundaram B, and Wallace L (2015). Groundwater Hydrochemical Characterisation of the Surat Region and Laura Basin Queensland. Final technical report for the National Collaboration Framework Hydrochemical Characterisation Project: 218.
- Reagan MT, Moridis GJ, Keen ND, and Johnson JN (2015). Numerical simulation of the environmental impact of hydraulic fracturing of tight/shale gas reservoirs on near-surface groundwater: Background, base cases, shallow reservoirs, short-term gas, and water transport. Water Resources Research 51: 2543–2573.
- Reed M, French D, and Rines H (1994). Numerical simulation of biological effects of oil spills. Journal of Advanced Marine Technology Conference 11: 65–90.
- Rice CA, Ellis MS, and Bullock JH Jr (2000). Water co-produced with coalbed methane in the Powder River Basin, Wyoming: preliminary compositional data. USGS Open File-Report 00-372. https://pubs.usgs.gov/of/2000/ofr-00-372/results.html#TOP.
- Rodvelt G (2014). Vertical Well Construction and Hydraulic Fracturing for CBM Completions. Coal Bed Methane. Elsevier Inc. <u>http://doi.org/10.1016/B978-0-12-800880-5.00006-1</u>.
- Rogers RE (1994). Coalbed methane : principles and practice. Englewood Cliffs, N.J: PTR Prentice Hall.
- Rogers JD, Burke TL, Osborn SG, and Ryan JN (2015). A Framework for Identifying Organic Compounds of Concern in Hydraulic Fracturing Fluids Based on Their Mobility and Persistence in Groundwater. Environmental Science and Technology Letters 2: 158–164.
- Rutovitz J, Harris S, Kuruppu N, and Dustan C (2011). Drilling down. Coal seam gas. A background paper: Prepared for the City of Sydney by the Institute for Sustrainable Futures, University of Technology, Sydney.
- Safe Work Australia (2012) Guidance on the Interpretation of Workplace Exposure Standards for Airborne Contaminants, accessed in July 2016,

http://www.safeworkaustralia.gov.au/sites/SWA/about/Publications/Documents/680/Guidance_Interpretation_W orkplace Exposure Standards Airborne Contaminants%20.pdf>.

- Sanford W (2010). Calibration of models using groundwater age. Hydrogeology Journal 19: 13–16. doi:10.1007/s10040-010-0637-6.
- Santos (2013). Appendix E Golder supporting hazard ranking information. Santos GLNG Project. 626 pp.
- Santos (2014). Santos GLNG upstream hydraulic fracturing risk assessment Compendium of assessed fluid systems. Viewed 24 March 2016, http://www.santoswaterportal.com.au/media/pdf1876/compendium-assessed-fluidsystems.pdf.

- Santos (2016). Santos GLNG Gas Field Development Program. Water quality management. Preparted by EHS Support Pty Ltd.
- Savostianov NA (1991). Part 2. Advances in Cased Hole Logging and Completion Technology. OnePetro. 13th World Petroleum Congress, 20-25 October, Buenos Aires, Argentina. Paper WPC-24154.
- Sawamura S, Kitamura K, and Taniguchi Y (1989). Effects of pressure and temperature on the solubilities of benzene and alkylbenzenes in water. Journal of Physical Chemistry 93: 4931-4935.
- Sawamura S, Nagaoka K, Machikawa T (2001). Effects of pressure and temperature on the solubility of alkylbenzenes in water: volumetric property of hydrophobic hydration. Journal of Physical Chemistry 105: 2429-2436.
- Schlumberger Water Services (2012). Namoi Catchment Water Study Independent Expert Final Study Report, prepared by Schlumberger Water Services (Australia) Pty Ltd. for the Department of Trade and Investment, Regional infrastructure and Services, NSW.
- Schoderboeck L, Muhlegger S, Losert A, Gausterer C, and Hornek R (2011). Effects assessment: boron compounds in the aquatic environment. Chemosphere 82: 483-487.
- Scott S, Anderson B, Crosdale P, Dingwall J, and Leblang G (2007). Coal petrology and coal seam gas contents of the Walloon Subgroup – Surat Basin, Queensland, Australia. International Journal of Coal Geology 70: 209-222.

Scow KM and Johnson CR (1997). Effect of sorption on biodegradation of soil pollutants. Advances in Agronomy 58: 56.

- Seybold CD (1994). Polyacrylamide review: Soil conditioning and environmental fate, Communications in Soil Science and Plant Analysis 25(11-12): 2171-2185.
- Sharma P, Mayes MA, and Tang G (2013). Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils. Chemosphere 92(8): 993-1000.
- Shaw M (2010). Stream ecosystem health response to coal seam gas water release: Hazard characterisation. Brisbane: Department of Science, Information Technology, Innovation and the Arts.
- Shulka OP and Bhattacharyya PK (1968). Microbial transformation of terpenes: Part XI Pathways of degradation of alpha and beta pinenes in a soil pseudomonad (PL-strain). Indian Journal of Biochemistry 5(3): 92–101.

Sigma-Aldrich (2014). Material Safety Data Sheet for 2-Bromo-2-nitro-1,3-propanediol; St. Louis, MO, USA, 2014.

- Simane GS, Maledi N, Ochieng A, Ndlovu S, Zhang J, and Walubita LF (2016). Coal-based adsorbents for water and wastewater treatment. Journal of Environmental Chemical Engineering 4: 2291-2312.
- Siskin M and Aczel T (1983). Pyrolysis studies on the structure of esters and phenols in coal. Fuel 62: 1321-1326.
- Smedley PL and Kinniburgh DG (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemstry 17: 517–568.
- Smith SD, Mathouchanh E and Mallants D (2016). Characterisation of fluid flow in aquitards using helium concentrations in quartz, Gunnedah Basin, NSW. CSIRO, Australia.
- Snoyeink VL, Weber Jr WJ, and Mark Jr HJ (1969). Sorption of phenol and nitropehnol by active carbon. Environmental Science and Technology 3: 918-926.
- Sposito G (1984). The surface chemistry of soils: Oxford University Press, New York, 234 pp.
- Stearman W, Taulis M, Smith J, and Corkeron M (2014). Assessment of Geogenic Contaminants in Water Co-Produced with Coal Seam Gas Extraction in Queensland, Australia: Implications for Human Health Risk. Geosciences 4: 219-239.
- Steep BE and McClure PD (2001). The effect of temperature on adsorption of organic compounds to soils. Canadian Geotechnology Journal 38: 46-52.
- Stumm W and Morgan JJ (1996). Aquatic Chemistry. Chemical equilibria and rates in natural waters. Third edition. John Wiley and Sons, New York, 1022 pages.
- Stumm W and Morgan JJ (1981). Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, John Wiley and Sons, New York, NY.
- Suckow A, Taylor A, Davies P, and Leaney F (2016). Geochemical baseline monitoring. Final Report. CSIRO, Australia.

- Sun Y and Clement TP (1999). A Decomposition Method for Solving Coupled Multi-Species Reactive Transport Problems. Transport in Porous Media 37: 327-346.
- Sun Y, Petersen JN, Clement TP (1999a). Analytical solutions for multiple species reactive transport in multiple dimensions. Journal of Contaminant Hydrology 35: 429-440.
- Sun Y, Petersen JN, Clement TP, Skeen RS (1999b). Development of analytical solutions for multispecies transport with serial and parallel reactions. Water Resources Research 35(1): 185-190.
- Svensson K, Darnerud PO, and Skerfving S (2005). A risk assessment of uranium in drinking water, National Food Administration of Sweden, Sweden.
- Swenberg JA, Kerns WD, Mitchell RI, Gralla EJ, and Pavkov KL (1980). Induction of squamous cell carcinomas of the rat nasal cavity by inhalation exposure to formaldehyde vapor. Cancer Research 40 (9): 3398–3402.
- Taylor SR (1964). Abundance of chemical elements in the continental crust: a new table. Geochimica et Cosmochimica Acta 28: 1273-1285.
- Tessier A (1992). Sorption of trace elements on natural particles in oxic environments. Chapter 11 in Environmental particles, Volume 1. Buffle J. and Van Leeuwen H.P. Eds. Lewis, Boca Raton.
- TGA (2012). The Poisons Standard 2012, Standard for the Uniform Scheduling of Medicines and Poisons. Therapeutic Goods Administration.
- Thibault DH, Sheppard MI and Smith PA (1990). A critical compilation and review of default soil solid/liquid partition coefficients, Kd, for use in environmental assessments. Atomic Energy of Canada Limited. Whiteshell Nuclear Research Establishment Pinawa, Manitoba, Canada.
- Thomas J Jr and Damberger H (1976). Internal surface area, moisture content, and porosity of Illinois coals: Variations with coal. Illinois State Geological Survey. Illinois State Geological Circular 493: 1-38.
- Toride N, Leji FJ, van Genuchten MTh (1999). The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.1. US Salinity Laboratory, ARS-USDA, Riverside California.
- Tóth J (1962). A theory of groundwater motion in small drainage basins in central Alberta, Canada. Journal of Geophysical Research 67(11): 4375-4388.
- Tóth J (1963). A theoretical analysis of groundwater flow in small drainage basins. Journal of Geophysical Research 68(16): 4795-4812.
- Totterdell JM, Moloney J, Korsch RJ, and Krassay AA (2009). Sequence stratigraphy of the Bowen-Gunnedah and Surat Basins in New South Wales. Australian Journal of Earth Sciences, Special Issue: Evolution of the Bowen, Gunnedah and Surat Basins, eastern Australia Volume 56 (3): 433-459.
- TOXNET. Toxicology data network. NIH US National Library of Medicine. https://toxnet.nlm.nih.gov/; accessed May 2016.
- Treccani V, Walker N, and Wiltshire GH (1954). The metabolism of naphthalene by soil bacteria. Journal of General Microbiology 11: 341-348.
- United Nations (2011). Globally Harmonised System of Classification and Labelling of Chemicals (GHS), United Nations Economic Commission for Europe, 4th revised edition.
- US Congress (2011). Chemicals used in hydraulic fracturing. United States House of Representatives Committee on Energy and Commerce. April 2011, 29 pp.
- US EPA (1992). Guidelines for Exposure Assessment. Risk Assessment Forum. U.S. Environmental Protection Agency, Washington, DC: 139.
- US EPA (1994a). Handbook of Ground Water and Wellhead Protection, US Environmental Protection Agency, Report EPA/625/R-94001, 288 p.
- US EPA (1994b). Registration Eligibility Decision (RED) Limonene. US Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (EPA-738-R-94-034). U.S. Government Printing Office: Washington, DC, USA.
- US EPA (1994c). Determination of groundwater dilution attenuation factors for fixed waste site areas using EPACMTP. Background document. EPA office of solid waste. Appendix E.

- US EPA (1995a). National primary drinking water regulations. Acrylamide. United States Environmental Protection Agency, Office of Water 4601 EPA 811-F-95-004a-T October 1995.
- US EPA (1995b). Reregistration Eligibility Decision (RED) Bronopol. United States Environmental Protection Agency. Prevention, Pesticides And Toxic Substances (7508W), EPA738-R-95-029 October 1995.
- US EPA (1998a). Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. EPA/600/R-98/128 September 1998.
- US EPA (1998b). Reregistration Eligibility Decision (RED) Methylisothiazolinone. United States Environmental Protection Agency. Prevention, Pesticides and Toxic Substances (7508C), EPA738-R-98-012 October 1998.
- US EPA (1999a). Understanding variation in partition coefficient, Kd values. Volume II: Review of geochemistry and available Kd Values for cadmium, caesium, chromium, lead, plutonium, radon, strontium, thorium, tritium (3H), and uranium. US Environmental Protection Agency report EPA 402-R-99-004B, 341 pages.
- US EPA (1999b). Understanding variation in partition coefficient, Kd, values. Volume I: The Kd model, methods of measurement, application of geochemical reaction codes. EPA 402-R-99-004A.
- US EPA (2004a). Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs. No. EPA/816/R-04/003. Washington, DC: US Environmental Protection Agency, Office of Water.
- US EPA (2004b). Understanding variation in partition coefficient, Kd values. Volume III: Review of Geochemistry and Available Kd Values for americium, arsenic, curium, iodine, neptunium, radium, and technetium. US Environmental Protection Agency report EPA 402-R-04-002C, 188 pages.
- US EPA (2005). Toxicological Review of Barium and Compounds. United States Environmental Protection Agency, EPA/635/R-05/001.
- US EPA (2006). Ohio EPA Aquatic Life Water Quality Criteria Factsheet. https://www.epa.gov/sites/production/files/2015-06/documents/oh_al_337_03012006.pdf (accessed 20 June 2016)
- US EPA (2008a). National Primary Drinking Water Standards, United States Environmental Protection Agency, https://safewater.zendesk.com/hc/en-us/sections/202366558
- US EPA (2008b). Health Effects Support Document for Boron, USEPA, Office of Water Health and Ecological Criteria Division, EPA-822-R-08-002, January 2008.
- US EPA (2009). Screening-level hazard characterization Monoterpene Hydrocarbons Category. Hazard characterization document.
- US EPA (2010). Hydraulic fracturing research study. Factsheet. Office of Research and Development, June 2010.
- US EPA (2011). Plan to study the potential impacts of hydraulic fracturing on drinking water resources. Office of Research and Development, November 2011.
- US EPA (2012a). Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. Progress Report EPA 601/R-12/011. US Environmental Protection Agency Office of Research and Development Washington, DC
- US EPA (2012b). The Estimation Programs Interface (EPI) Suite. ECOSAR.
- US EPA (2013). Summary of the Technical Workshop on Well Construction / Operation and Subsurface modeling (April 16-17, 2013) and Subsurface Modeling Technical Follow-up Discussion (June 3, 2013).
- US EPA (2016a). Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Watr Cycle on Drinking Water Resources in the United States. Office of Research and Development, Washington, DC. EPA/600/R-16/236Fa.
- US EPA (2016b). EPA-Expo-Box (A Toolbox for Exposure Assessors), available at http://www.epa.gov/expobox.
- US EPA (2016c). ECOTOX User Guide: ECOTOXicology Knowledgebase System. Version 4.0. Available: http://www.epa.gov/ecotox/ (accessed 23 June 2016)
- US EPA (2016d). Office of Pesticide Programs database. Office of Prevention, Pesticides, and Toxic Substances. Office of Pesticide Programs. Washington, D.C. January 23, 2004. Available from: http://www.ipmcenters.org/ecotox/, Accessed: 23 June 2016.
- US EPA Pesticides reregistration status (https://archive.epa.gov/pesticides/reregistration/web/html/status.html)

- Van Aken B, Yoon JM, and Schnoor JL (2004). Biodegradation of Nitro-Substituted Explosives 2,4,6-Trinitrotoluene, Hexahydro-1,3,5-Trinitro-1,3,5-Triazine, and Octahydro-1,3,5,7-Tetranitro-1,3,5-Tetrazocine by a Phytosymbiotic Methylobacterium sp. Associated with Poplar Tissues (Populus deltoides _ nigra DN34). Applied and Environmental Microbiology 70: 508–517.
- van Genuchten MTh (1985). Convective-dispersive transport of solutes involved in sequential first-order decay reactions. Computers and Geosciences 11(2): 129-147.
- van Genuchten MTh, Simunek J, Leji FJ, Toride N, Segna M (2012). STANMOD: Model use, calibration and validation. Transactions of the American Society of Agricultural and Biological Engineers 55(4): 1353-1366.
- van Stempvoort D and Biggar K (2008). Potential for bioremediation of petroleum hydrocarbons in groundwater under cold climate conditions: a review. Cold Regions Science and Technology 53: 16-41.
- Waggy GT, Conway RA, Hansen JL, and Blessing RL (1994). Comparison of 20-d BOD and OECD closed-bottle biodegration test. Environmental Toxicology and Chemistry 13(8):1277-1280.
- Wagner J, Watts SA, and Kent DC (1985). PLUME3D: three-dimensional plumes in uniform groundwater flow. Prepared for Robert S. Kerr Environmental Research Laboratory U.S.E nvironmental Protection Agency Ada, OK.
- Walker JE and Kaplan DL (1992). Biological degradation of explosives and chemical agents. Biodegradation 3(2-3): 369-385.
- Wang WW (1991). Aerobic Soil Metabolism of 14C RH-651; Xenobiotic Laboratories, Inc (XBL), Plainsboro, New Jersey, USA, XBL Report N°. RPT0045, Rohm and Haas Technical Report N°. 34-91-03 (April 11, 1991), Unpublished.
- Wang HF, Provan GH, and Helliwell K (2002). Determination of bronopol and its degradation products by HPLC. Journal of pharmaceutical and biomedicine analysis. 29 (1-2): 387-392.
- Wang L, Martens E, Jacques D, De Cannière P, Berry JA, and Mallants D (2009). Review of sorption values for the cementitious near field of a near-surface radioactive waste disposal facility, NIROND-TR 2008-23 E.
- Ward WT (1999). Soils and landscapes near Narrabri and Edgeroi, NSW, with data analysis using fuzzy k-means. CSIRO Land and Water Technical Report 22/99.
- Warne MStJ, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW and Stauber JL (2015). Revised Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants. Prepared for the Council of Australian Government's Standing Council on Environment and Water (SCEW). Department of Science, Information Technology and Innovation, Brisbane, Queensland. 43 pp.
- Warner NR, Jackson RB, Darrah TH, Osborn SG, Down A, Zhao K, White A, and Vengosh A (2012a). Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. Proceedings of the National Academy of Sciences, 109: 11961-11966. http://dx.doi.org/10.1073/pnas.1121181109
- Warner NR, Jackson RB, Darrah TH, Osborn SG, Down A, Zhao K, White A, and Vengosh A (2012b). Reply to Engelder: Potential for fluid migration from the Marcellus Formation remains possible. Proceedings of the National Academy of Sciences: 1.
- Warpinski N (2009). Microseismic Monitoring: Inside and Out. Journal of Petroleum Technology 61(11): 80–85. http://doi.org/10.2118/118537-MS.
- Weissmahr KW Haderlein SB Schwarzenbach RP Hany R, and Nüesch R (1997). In situ spectroscopic investigation of adsorption mechanisms of nitroaromatic compounds at clay minerals. Environmental Science and Technology 31(1): 240-247.
- Wen Q, Chen Z, Zhao Y, Zhang H, and Feng Y (2010). Biodegradation of polyacrylamide by bacteria isolated from activated sludge and oil-contaminated soil. Journal of Hazardous Materials 175(1–3): 955-959.
- Wexler EJ (1992). Analytical solutions for one-, two-, and three-dimensional solute transport in groundwater systems with uniform flow. Techniques of Water-Resources Investigations of the United States Geological Survey.
- WHO (1998a). Environmental Health Criteria Document No. 204: Boron (7740-42-8). International programme on chemical safety, World Health Organization, Geneva. 203 pages.
- WHO (1998b). International Programme on Chemical Safety Concise International Chemical Assessment Document No. 5. Limonene. World Health Organization, Geneva. ISBN 92 4 153005 7.

- WHO (1998c) 2-Butoxyethanol. Concise International Chemical Assessment Document 10, World Heath Organisation, Geneva.
- WHO (1990). Environmental health criteria 107, Barium. Published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization. http://www.inchem.org/documents/ehc/ehc107.htm
- WHO (2001). Arsenic and Arsenic Compounds, Environmental Health Criteria 224. World Health Organisation, Geneva.
- WHO (2003). Arsenic in drinking-water: Background document for development of WHO Guidelines for Drinking-water, World Health Organisation, Geneva.
- WHO (2004a). Barium in drinking-water, Background document for development of WHO Guidelines for Drinking-Water Quality, World Health Organisation, Geneva. WHO/SDE/WSH/03.04/76.
- WHO (2004b). Boron in Drinking Water. Background document for development of WHO Guidelines for Drinking-water Quality, World Health Organisation, Geneva. WHO/SDE/WSH/03.04/54.
- WHO (2004c). Uranium in drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality, World Health Organisation, Geneva.
- WHO (2011). Guidelines for Drinking-water Quality 4th Edition. World Health Organization. Geneva.
- WHO (2012). Uranium in drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality, World Health Organisation, Geneva.
- Wolhart SL, Harting TA, Dahlem JE, Young TJ, Mayerhofer MJ, and Lolon EP (2006). Hydraulic fracture diagnostics used to optimize development in the Jonah Field. Proceedings – Society of Petroleum Engineers Annual Technical Conference and Exhibition, 4, 2305–2316. http://doi.org/10.2118/102528-MS.
- Wu B, Doble R, Turnadge C, and Mallants D (2016). Bore and well induced inter-aquifer connectivity: a review of literature on failure mechanisms and conceptualisation of hydrocarbon reservoir-aquifer failure pathways. Prepared by the Commonwealth Scientific and Industrial Research Organisation CSIRO, Canberra.
- Wylde JJ and O'Neil B (2011). Environmentally-acceptable replacement of 2-butoxyethanol: A high performance alternative for fracturing applications. Society of Petroleum Engineers (141099): 16.
- Yediler A, Kettrup A, NüBlein F, and Korte F (1991). Mobility of o-cresol in sandy soil in the presence of linear alkylbenzene sulfonate. Toxicological and Environmental Chemistry 31(1): 119-125.
- Zheng H, Feng XT, and Pan PZ (2015). Experimental investigation of sandstone properties under CO2-NaCl solution-rock interactions. International Journal of Greenhouse Gas Control 37: 451-470.
- Zurimendi JA, Guerrero SJ, and Leon V (1984). The determination of the degree of hydrolysis in poly(acrylamides): simple methods using C13 nmr, and elementary analysis. Polymer 25(9): 1314-1316.