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

Release of geogenic contaminants from Australian coal seams: experimental studies

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National Industrial Chemicals Notification and Assessment Scheme
Communications Branch
Department of Health
GPO Box 9848
CANBERRA ACT 2601
Australia

Or by email to: copyright@health.gov.au

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Front cover photos

Image (left to right): Coal seam gas well pad, 2013, ‘Spring Gully’, Queensland (© Department of the Environment, courtesy Origin Energy); Coal seam gas well head, pump, and pipe works, 2013, Spring Gully, Queensland (© Department of the Environment, courtesy Origin Energy); Coal seam gas well construction, 2010, ‘Fairview’, Queensland (© Department of the Environment, courtesy Santos).

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Summary

Concerns surrounding the use of hydraulic fracturing as part of the coal seam gas extraction process have mainly centered on the potential effects of a range of industrial chemicals that are the constituents of hydraulic fracturing fluids. However, as part of their natural mineral composition, coal seams are known to contain a number of contaminants that have the potential to be mobilised by hydraulic fracturing activities. These so-called geogenic contaminants include trace elements (such as arsenic, manganese, barium, boron and zinc), radionuclides (e.g. isotopes of radium, thorium and uranium) and organic contaminants such as hydrocarbons and phenols. Some chemicals used in hydraulic fracturing have the potential to release or mobilise geogenic contaminants in the coal seam through the effects of chelating agents, acids, surfactants and solvents. Their release into water introduced into or naturally present in the coal seams raises concerns about potential impacts on both groundwater and the effect of flowback and produced water released to surface sites.

As a prelude to practical investigations, a detailed literature review was conducted (Apte et al. 2017). The review investigated geogenic contaminants of potential concern and the processes that may lead to their release during hydraulic fracturing and the production phase of coal seam gas operations. Overall, the review highlighted the paucity of data on geogenic contaminant concentrations in flowback and produced waters and emphasised a need for mechanistic studies to better understand the interactions between chemicals used in hydraulic fracturing chemicals and coal seams and the consequent implications for contaminant release and mobilisation.

The concentrations of geogenic contaminants released from a coal seam will depend on the composition of the hydraulic fracturing agents, groundwater composition and the nature of the coal seam undergoing gas extraction. It is therefore necessary to identify the potential geogenic elements / compounds in Australian coal seams, together with an understanding of the compounds that are likely to be released into flowback and produced water under hydraulic fracturing conditions. Practically, this is difficult to achieve through field-based investigations. Hence this report describes a laboratory-based study that investigated the potential for release of geogenic contaminants from coal samples taken from eight locations across Eastern Australia. This involved the development and application of leach tests which were designed to assess the release of geogenic substances and also provide some information on the physico-chemical factors affecting contaminant release. The tests were designed to provide upper bound estimates of contaminant release.

The aims of the study were to:

- generate data on the concentrations of trace metals and radioactive substances in selected Australian coal seam source materials
- identify potential inorganic contaminants that may be released from coal seams
- explore development of analytical methodologies for the determination of organic geogenic substances and obtain preliminary information on their occurrence in coal leachates
- develop and apply laboratory leach tests that allow the chemical screening of contaminants likely to be released from Australian coal seams during the process of hydraulic fracturing of coal seams.

The approach adopted in this study was to investigate the release of potential contaminants of concern from selected coal samples representative of coal seams that are currently, or

may in the future, be subject to gas extraction. A number of chemical leach tests were developed and applied. The leaching agents used in this study included dilute acid, pH buffers amended with the metal complexing agent citrate, and a synthetic groundwater. Based on available literature information, a synthetic hydraulic fracturing fluid was also prepared and used in combination with high pressure and temperature, as part of the suite of leaching tests. The synthetic hydraulic fracturing fluid was designed to provide an upper bound composition of a hydraulic fracturing mixture in terms of the concentrations of active ingredients.

Over 65 trace elements were quantified in the leachate samples and their concentrations compared to water quality guideline values for aquatic ecosystem protection (where available). Radium-226 activities were also quantified.

While the characterisation of inorganic geogenic contaminants is relatively straightforward, the analysis and quantification of organic contaminants in complex environmental matrices is not. The organics phase of this project was therefore more exploratory in nature. In particular, the organics phase aimed to identify methodological problems encountered during the analysis of organic geogenic compounds and to also provide some preliminary data on organic compounds that may be released from coal samples.

Based on the laboratory studies, contaminants of potential concern were subsequently identified and recommendations for further investigations made.

The conclusions of the study are listed below.

1. Detectable concentrations of over 60 trace elements were observed in the laboratory-based leach tests conducted on a range of Australian coal samples. These data may be viewed as upper bound estimates of geogenic contaminant release from coal seams undergoing gas extraction.
2. Large variability was observed between coal types, in the measured trace element and organics concentrations in both the whole coals and in their leachates. This emphasises the need for site-specific investigations to ascertain the risk posed by geogenic contaminants at a given coal seam gas operation.
3. Based on their measured concentrations in the laboratory-based leaching studies and comparison with surface water quality benchmarks for aquatic ecosystem protection, the following inorganic geogenic contaminants have been identified as priorities for further investigations: aluminium, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, lead, manganese, nickel, selenium, silver, thallium, uranium, vanadium and zinc.
4. It should be noted that water quality benchmarks are not available for a number of trace elements that were found in the leachates (e.g. barium).
5. Radionuclide concentrations (radium, thorium and uranium) in the leachates generated from the coal samples tested were very low and, based on their radioactive properties, were below concentrations of regulatory concern. However, this does not preclude the preconcentration of radionuclides in precipitates forming in flowback and produced water ponds, pipeworks, or during water treatment (e.g. in micro-filtration filters and reverse osmosis membranes).
6. Phenol and cresols (methylphenols) were the most commonly detected compounds in coal samples leached with synthetic groundwater, particularly in the presence of the hydraulic fracturing chemicals. The median concentration of phenol in leachates (before dilution with groundwater) was 220±120 µg/L, which is below the water quality guideline

value of 320 µg/L for 95% species protection (ANZECC and ARMCANZ 2000). The median concentrations of o-cresols and m- plus p-cresols were 21 and 75 µg/L, respectively. However, these concentrations exceed the Canadian water quality guidelines for monohydric phenols (which include phenol and cresols among other compounds).

7. Higher concentrations of phenols and other low molecular weight total recoverable hydrocarbons in the C_{10}-C_{14} range were released on leaching of coal samples with synthetic groundwater mixed with hydraulic fracturing chemicals at high temperature and pressure compared to leaching with un-amended synthetic groundwater.
8. Based on gas chromatography-mass spectrometry library searches a further 14 organic compounds were identified in the coal leachates, but their origin (geogenic or not) is not clear. Generally, a greater number of compounds (as indicated by the C_{10}-C_{14} total recoverable hydrocarbon load) were detected in the presence of hydraulic fracturing. The nature and concentration of new compounds formed through the interaction of coal and fracturing fluid needs further investigation. Furthermore, the ecological relevance, in terms of their environmental fate and ecological effects, of the identified organic compounds is not well understood and needs to be addressed.
9. The elevated temperature and pressure in groundwater during the hydraulic fracturing process appears to play a role in the mobilisation of organic substances. However, the effects were found to be compound specific. A systematic investigation is needed under conditions relevant to hydraulic fracturing in Australia.

The complex mixtures of organic chemicals released from coals present significant analytical challenges including achieving adequate sensitivity and elimination interference during analysis. Further work is needed to develop more sensitive, specific and robust analytical methods.

Abbreviations

General abbreviations	Description
ANSTO	Australian Nuclear Science and Technology Organisation
ANZECC and ARMCANZ	Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand
ASE	Accelerated solvent extraction
BTEX	Benzene, toluene, ethylbenzene, xylenes
CCME	Canadian Council of Ministers of the Environment
CAS	Chemicals Abstracts Service
CSG	Coal seam gas – naturally occurring gas in coal seams
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DERM	Department of Environment and Resource Management
DoE	Department of the Environment
GC-MS	Gas chromatography-mass spectrometry
HFF	Hydraulic fracturing fluid
HLB	Hydrophilic-lipophilic balance
ICP-AES	Inductively-coupled atomic emission spectrometry
ICP-MS	Inductively-coupled mass spectrometry
K_{ow}	Octanol-water partition coefficient
LOD	Limit of detection
LOR	Limit of reporting
MSDS	Material Safety Data Sheet
MS/MS	Mass spectrometry/mass spectrometry
NATA	National Association of Testing Authorities
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NIST	National Institute of Standards (United States)
NMI	National Measurement Institute
NSW	New South Wales
OWS	Office of Water Science
PAH	Polycyclic aromatic hydrocarbon
Qld	Queensland
SGW	Synthetic groundwater

General abbreviations	Description
SIM	Selected ion monitoring
SPE	Solid phase extraction
SRC	Syracuse Research Corporation
TDS	Total dissolved solids
TRH	Total recoverable hydrocarbons
US EPA	United States Environmental Protection Agency
WHO	World Health Organisation

Symbols

Units, chemicals and symbols	Description
Bq	Becquerel
°C	Degrees Celsius
g	Grams
hr	Hours
L	Litre
m	Metre
M	Molar concentration
m/v	Mass per volume
min	Minutes
Pa	Pascal
ppb	Parts per billion; equivalent to µg/L or µg/kg
ppm	Parts per million; equivalent to mg/L or mg/kg
psi	Pounds per square inch
RPM	Revolutions per minute
v/v	Volume per volume
Ω	Ohms
Ag	Silver
Al	Aluminium
As	Arsenic
B	Boron
Ba	Barium
Be	Beryllium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Cl^-	Chloride ion
Co	Cobalt
Cr	Chromium
Cs	Caesium

Units, chemicals and symbols	Description
Cu	Copper
Dy	Dysprosium
Er	Erbium
Eu	Europium
Fe	Iron
Ga	Gallium
Gd	Gadolinium
HCl	Hydrogen chloride (hydrochloric acid)
HCO_3^-	Bicarbonate ion
Hf	Hafnium
Ho	Holmium
In	Indium
Ir	Iridium
K	Potassium
La	Lanthanum
Li	Lithium
Lu	Lutetium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na^+	Sodium ion
Na_2SO_4	Sodium sulfate
NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
Nb	Niobium
Nd	Neodymium
Ni	Nickel
Os	Osmium
P	Phosphorus
Pb	Lead
Pt	Platinum
Rb	Rubidium
Rh	Rhodium

Units, chemicals and symbols	**Description**
Ru	Ruthenium
S	Sulfur
Sb	Antimony
Sc	Scandium
Se	Selenium
Sm	Samarium
Sn	Tin
Sr	Strontium
Ta	Tantalum
Tb	Terbium
Te	Tellurium
Th	Thorium
Ti	Titanium
Tl	Thallium
Tm	Thulium
U	Uranium
V	Vanadium
W	Tungsten
Yb	Ytterbium
Zn	Zinc
Zr	Zirconium
^{212}Bi	Bismuth-212, radioactive isotope of bismuth
^{214}Bi	Bismuth-214, radioactive isotope of bismuth
^{137}Cs	Caesium-137, radioactive isotope of caesium
^{40}K	Potassium-40, radioactive isotope of potassium
^{210}Pb	Lead-210, radioactive isotope of lead
^{226}Ra	Radium-226, radioactive isotope of radium
^{228}Ra	Radium-228, radioactive isotope of radium
^{228}Th	Thorium-228, radioactive isotope of thorium
^{208}Tl	Thallium-208, radioactive isotope of thallium
^{238}U	Uranium-238, radioactive isotope of uranium

Glossary

Term	Description
Alkane Alkene/Alkyne	Hydrocarbons containing single/double/triple bonds between carbon atoms
Amine	Organic compounds with a subunit containing nitrogen
Anthropogenic chemical	A chemical that has been industrially produced
Aromatic hydrocarbons	Hydrocarbons with carbon atoms arranged in a ring formation, with alternating single and double bonds; benzene is the basic aromatic sub-unit
Bottle roller	A piece of laboratory equipment which is designed rolls bottles which are placed on the roller on their sides, thereby mixing their contents
Carcinogen	A substance directly involved in causing cancer
Chelation	A particular way that ions and molecules can strongly bind metal ions
Chemical screening	A systematic series of chemical analyses or assessments that are performed in order to detect unwanted substances or specific attributes
Compton suppression gamma spectrometry	A specialized spectroscopic technique for measuring gamma rays emitted from radionuclides
Co-solvent	An additional solvent added to a solution to greatly enhance the ability to dissolve a solute
Cresols	Any of three isomeric organic compounds commonly found in coal-tar creosote. Cresols are methylphenols (hydroxytoluene isomers) and are widely used as disinfectants
Florisil® column	Florisil® columns are used in analytical chemistry to removed unwanted molecules from solution prior to chemical analysis. A small glass or plastic column is packed with Florisil® powder and the solution is passed through the column. Florisil® is a hard powdered magnesia-silica gel manufactured in the United States by U.S. Silica Company. It is particularly effective in removing polar molecules from solutions
Flowback water	The fluid that flows back, or is pumped back, to the surface following hydraulic fracturing but prior to gas production
Formation water	Naturally occurring water that is within or surrounding the coal, rock or other formations underground
Gas chromatography-mass spectrometry	A gas chromatograph equipped with mass spectrometer required for the analysis of a range of organic compounds such as phenolic compounds
Geogenic chemical	A naturally-occurring chemical originating, for example, from geological formations
Heterocycle	An aromatic sub-unit where atoms other than carbon (such as oxygen or nitrogen) replace carbon atoms

Term	Description
Hydraulic fracturing	Also known as ‘fracking’, ‘fraccing’, or ‘fracture stimulation’, is the process by which hydrocarbon (oil and gas) bearing geological formations are ‘stimulated’ to enhance the flow of hydrocarbons and other fluids towards the well. The process involves the injection of fluids, gas, proppant and other additives under high pressure into a geological formation to create a network of small fractures radiating outwards from the well through which the gas, and any associated water, can flow.
Hydraulic fracturing fluid	A fluid injected into a well under pressure to create or expand fractures in a target geological formation (to enhance production of natural gas and/or oil). It consists of a primary carrier fluid (usually water), a proppant and one or more additional chemicals to modify the fluid properties
Hydrophilic	Having an affinity for water; readily absorbing or dissolving in water
Hydrophobic	Lacking affinity for water; tending to repel and not absorb water; tending not to dissolve in or mix with or be wetted by water
ICP-AES	Inductively coupled plasma-atomic emission spectrometry - a highly sensitive spectroscopic technique that is able to simultaneously analyse a number of elements in liquid samples
ICP-MS	Inductively coupled plasma-mass spectrometry - a highly sensitive analytical technique that is able to simultaneously analyse a number of elements in liquid samples. ICP-MS is more sensitive than ICP-AES as it is based on mass spectrometry rather than the detection of light emission
Leach tests	Laboratory tests applied to solids whereby the solid is contacted with a solution containing chemicals for a fixed period of time under standardised conditions. Substances released from the solid into the solution are measured at the end of the test
Leachate	The filtered solution that is prepared at the end of the leach test. Solids are normally removed from the leachate by filtration or centrifugation
Limit of detection	The minimum concentration of an analyte that can be identified, measured, and reported with 95% confidence that the analyte concentration is greater than zero. In this work the limit of detection is calculated as 3 time the standard deviation of several analytical blank measurements
Limit of reporting	The lowest concentration at which an analyte can be detected in a sample and its concentration can be reported with a reasonable degree of accuracy and precision. The limit of reporting varies between laboratories and analytical methods and is typically calculated as ten times the standard deviation of several analytical blank measurements
Matrix	In chemical analysis, matrix refers to the components of a sample other than the chemical component of interest. The matrix can have a considerable effect on the way the analysis is conducted and the quality of the results obtained; such effects are called matrix effects
Mass spectrometry	Mass spectrometry (MS) is an analytical chemistry technique that helps identify the amount and type of chemicals present in a sample by measuring the mass-to-charge ratio and abundance of ions generated from the chemicals under investigation
Phenols or phenolic compounds	A class of chemical compounds consisting of a hydroxyl group (—OH) bonded directly to an aromatic hydrocarbon group. The simplest of the class is phenol, which is also called carbolic acid (C_6H_5OH).

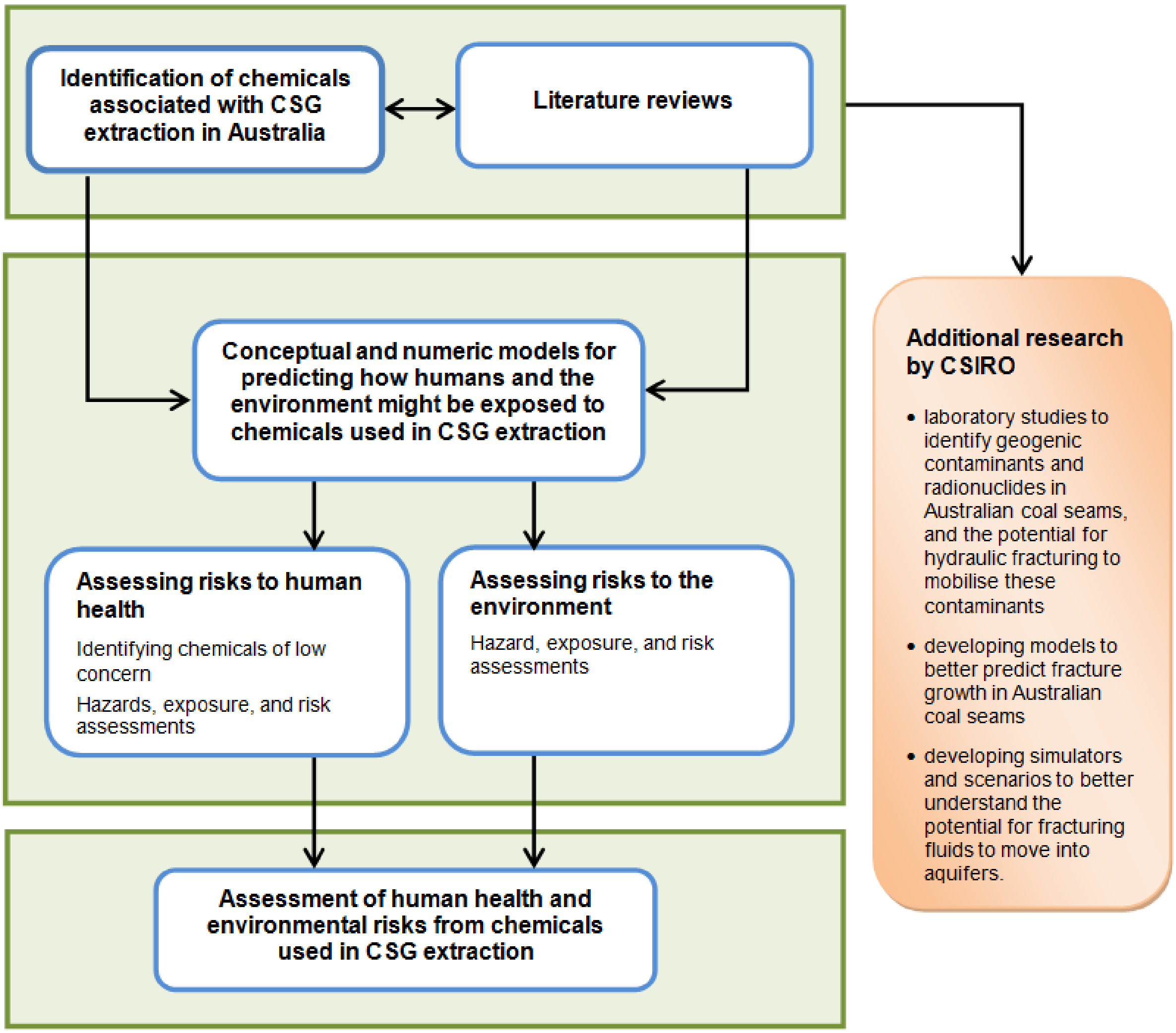
Term	Description
Pre-concentration	The concentration (enrichment) of a trace material prior to an analysis
Produced water	Water that is pumped out of the coal seams to release the natural gas during the production phase. Some of this water is returned fracturing fluid and some is natural ‘formation water’ (often salty water that is naturally present in the coal seam). This produced water moves through the coal formation to the well along with the gas, and is pumped out via the wellhead
Proppant	A component of the hydraulic fracturing fluid comprised of sand, ceramics or other granular material that ‘prop’ open fractures to prevent them from closing when the injection pressure is stopped
Surfactant	Used during the hydraulic fracturing process to decrease liquid surface tension and improve fluid movements
Sorption	The process where one substance binds to another either through absorption (incorporation into a solid) or adsorption (binding to surface of a solid)

1 Introduction

1.1 National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia

The National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia was commissioned by the Australian Government in June 2012, informed by advice from the Independent Expert Scientific Committee on Coal Seam Gas and Large Coal Mining Development (IESC).

The project aimed to assess the risks to human health and the environment from chemicals used to extract coal seam gas. It was conducted in stages, as outlined in Figure 1.1.



Note. Orange box indicates the stage of the assessment that is relevant to this report.

Figure 1.1 Stages of the National Assessment of Chemicals Associated with Coal Seam Gas Extraction in Australia

The initial stage of the project was an extensive review of available literature, covering topics such as coal seam gas extraction, including hydraulic fracturing and drilling processes, environmental risks, human health impacts, risk modelling techniques, fracture growth, well integrity issues, and naturally occurring geogenic contaminants in Australian coals.

A next task was to identify the chemicals used to extract coal seam gas in Australia. The primary method was a voluntary industry survey, supplemented by a review of publicly reported information. The identified chemicals then formed the basis for the project's subsequent risk assessment processes.

The third stage of the project focused on developing conceptual models to show how humans and the environment might be exposed to the chemicals used to extract coal seam gas in Australia. These were used to inform the development of numerical models and simulators using regional data to help predict potential concentrations over time of the chemicals used in coal seam gas extraction in soils, surface water, and shallow groundwater.

The risk characterisation and assessment stage utilised nationally and internationally agreed risk assessment processes. This meant that the assessment of human health and environmental risks adopted different methodologies. In both cases, the risk characterisation was informed by consideration of the hazards associated with each of the chemicals being assessed, potential short and long-term exposure pathways, and relevant human and environmental receptors.

The risk characterisation process included assessment of the public, occupational and environmental risks arising from the use of drilling and fracturing chemicals based on current Australian work practices, and included activities such as:

- chemical handling, storage, transport, mixing, and injection
- management of flowback water
- management of produced water from coal seam gas wells (including activities such as transport from the well site, piping, storage, treatment, and waste disposal)
- accidental discharges to surface water, soils, and shallow groundwater from leaks, spills, and pond overflows.

Results, findings and associated recommendations from the risk assessments are brought together in a final report.

Issues that were beyond the scope of the project included:

- impacts of drilling and hydraulic fracturing chemicals on deeper groundwater systems (such as confined aquifers)
- the human health and environmental impacts associated with geogenic chemicals
- fugitive emissions to the atmosphere of geogenic gases (such as methane)
- other chemicals used at coal seam gas sites (such as diesel fuels and machinery lubricants)
- risks from chemicals used to extract other forms of unconventional gas.

Funded and managed by the Australian Government's Office of Water Science (Department of the Environment), this project was a collaboration between the National Industrial Chemicals Notification and Assessment Scheme (NICNAS; lead agency), Commonwealth Scientific and Industrial Research Organisation (CSIRO), Chemical Assessment Section (Department of the Environment) and, in an advisory role, Geoscience Australia. The research teams drew on the expertise of scientists in the fields of chemistry, hydrogeology, hydrology, geology, toxicology, ecotoxicology, natural resource management and risk assessment.

1.2 Geogenic contaminants

Concerns surrounding the use of hydraulic fracturing as part of the coal seam gas extraction process have mainly centered on the potential effects of a range of industrial chemicals that are the constituents of hydraulic fracturing fluids. However, coal seams are also known to contain a number of contaminants that have the potential to be mobilised during hydraulic fracturing activities (Apte et al. 2017). 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 waters introduced into or naturally present in the coal seams, raises concerns for their potential impacts both in natural groundwater and in flowback water that is brought to the surface.

As a first phase of this study, a detailed literature review was conducted (Apte et al. 2017). The review investigated geogenic contaminants of potential concern and the processes that may lead to their release during hydraulic fracturing and the production phase of coal seam gas operations. Overall, the review highlighted the paucity of data on geogenic contaminant concentrations in flowback and produced waters and emphasised the need for mechanistic studies to better understand the interactions of hydraulic fracturing chemicals with coal seams and the consequent implications for contaminant mobilisation.

The concentrations of geogenic contaminants mobilised from a coal seam will depend on the composition of the hydraulic fracturing agents, groundwater composition and the nature of the coal seam undergoing gas extraction. It is therefore necessary to identify the potential geogenic elements/compounds in Australian coal seams, together with an understanding of the compounds that are likely to be released into flowback water under hydraulic fracturing conditions. Practically, this is difficult to achieve through field-based investigations. Hence this report describes a laboratory-based study which investigated the potential for release of geogenic contaminants from coal samples taken from eight locations across Eastern Australia. This involved the development and application of leach tests which were designed to assess the release of geogenic contaminants and also provide some information on the physico-chemical factors affecting contaminant release.

The aims of the study were to:

- generate data on the concentrations of trace metals and radioactive substances in selected Australian coal seam source materials
- identify potential inorganic contaminants that may be released from coal seams
- explore the development of analytical methodologies for the determination of organic geogenic substances and obtain preliminary information on their occurrence in coal leachates
- develop and apply laboratory leach tests that allows for the screening of contaminants likely to be released from Australian coal seams during the process of hydraulic fracturing of coal seams.

Based on the laboratory studies, contaminants of potential concern were subsequently identified and recommendations for further investigations made.

2 Methodology

2.1 Study rationale

The approach adopted in this study was to investigate the release of potential contaminants of concern from selected coal samples representative of coal seams that are currently or may in the future be subject to gas extraction. Laboratory leaching tests that were designed to simulate upper bound estimates of geogenic contaminant release were developed and applied. The logic of this approach was as follows: if contaminants were not detected during these laboratory simulations which were conducted under deliberately harsh conditions, then they are unlikely to be detected in environmental samples.

While the characterisation of inorganic geogenic contaminants is relatively straightforward, the analysis and quantification of organic contaminants in complex environmental matrices is not. The organic contaminants phase of this project was therefore more exploratory in nature. Aside from providing some preliminary data on organic compounds that may be released from coal samples, it had the secondary goal of identifying methodological problems (e.g. matrix interferences) that may be encountered during the analysis of organic geogenic compounds.

The leaching tests applied during this study are summarised in Table 2.1. Given the relative ease of trace metals analysis by inductively coupled plasma-mass spectrometry (ICP-MS), a number of leach tests were applied to the coal samples (dilute acid, buffered solutions with/without citrate) and analysed for inorganic contaminants only. These tests are described in more detail in the ensuing sections. Dilute acid solutions are widely used in leaching studies applied to environmental matrices as they solubilise minerals and thereby release trace elements into solution. These leach tests were intended to give an upper bound estimate of trace element release from coals – actual concentrations in flowback or produced waters would also be influenced by dilution. Buffer solutions (pH 5 and pH 7) were used to simulate milder pH conditions that are more representative of those encountered during hydraulic fracturing. The metal complexing agent citrate, which is a common additive found in most hydraulic fracturing fluid formulations, was added to some of the buffer solutions in order to assess its effect on metal mobilisation.

Following method development, leach tests were carried out on the eight coal samples using the extractants detailed in Table 2.1. Over 65 trace elements were quantified in the leachate samples and their concentrations compared to water quality guideline values (where available). Uranium, thorium and Ra-226 concentrations were also quantified. However, for the organics studies, the leaching tests focused on aqueous solutions comprising a synthetic hydraulic fracturing fluid chemical mixture (HFF) diluted with synthetic groundwater (SGW) and compared with a SGW control (Table 2.1). The primary intention was to make a comparison between the relative leaching ability of saline groundwater and the same groundwater mixed with hydraulic fracturing fluid. These experiments were conducted at high pressure (10.3 MPa) and temperature (50ºC and 100ºC).

Leaching of coal at an elevated pressure (10.3 MPa) and temperature (100°C) was also designed to represent the upper bounds of temperature and pressure conditions that could occur during hydraulic fracturing operations. These temperature and pressure values were used as 'standard test conditions' during the organic geogenic leaching experiments. A survey of Australian coal seam gas company websites indicated the maximum coal seam depth that is currently exploited for coal seam gas extraction is around 1000 m. The average geothermal temperature gradients in Bowen, Galilee and Surat basins have been found to range from 43±13 to 84±23°C/km (Holgate & Gerner 2014), with hydraulic fracturing assumed to occur up to 1 km below the surface. Similarly, 10 MPa was considered to represent an approximate upper limit of pressures experienced during hydraulic fracturing (Zoback & Haimson 1983).

A synthetic hydraulic fracturing fluid (HFF) was prepared based on available information on typical hydraulic fracturing fluid composition. A detailed list of hydraulic fracturing fluid chemicals used in coal seam gas extraction in Australia is provided in the report by NICNAS (2016). The report contains useful information obtained through a voluntary survey of the coal seam gas industry. However, this information was not available at the time of this study and the composition for the hydraulic fracturing fluid was based on information publicly available from Halliburton (2014) (see Table 2.2). Only chemicals with a listed Material Safety Data Sheet (MSDS) could be identified and included. A gelling agent was not included in the mixture as this was regarded as a relatively inert component of the hydraulic fracturing fluid that would not influence the release of geogenic substances from coal samples. The highest individual chemical concentration in hydraulic fracturing fluids listed by Halliburton was also used. From this information, a synthetic hydraulic fracturing fluid was formulated that provided an upper bound composition of a hydraulic fracturing mixture in terms of the concentrations of active ingredients.

. The overall final composition of hydraulic fracturing fluid, listed in Table 2.2 represents a total chemical concentration of around 5% (m/v).

Table 2.1 Composition of the leach test solutions

Leach solution	**Components**	**Leach test conditions**	**Substances analysed**
Dilute hydrochloric acid	0.1 M hydrochloric acid (Merck, Tracepur) or 0.2 M hydrochloric acid (Narrabri sample only)	40°C, atmospheric pressure	Trace metals, inorganics, radionuclides
Synthetic groundwater (SGW) (pH 7)	750 mg/L sodium chloride, 750 mg/L sodium bicarbonate	40°C, atmospheric pressure	Trace metals, inorganics, radionuclides
SGW plus citrate at pH 7	750 mg/L sodium chloride, 750 mg/L sodium bicarbonate, 48 mg/L citric acid, 30 mg/L acetic acid	40°C, atmospheric pressure	Trace metals, inorganics, radionuclides
SGW plus citrate at pH 5	750 mg/L sodium chloride, 750 mg/L sodium bicarbonate, 48 mg/L citric acid, 155 mg/L acetic acid, 240 mg/L sodium acetate Sufficient 1.5 M nitric acid (Merck, Tracepur) to achieve pH 5 (sample dependent)	40°C, atmospheric pressure	Trace metals, inorganics, radionuclides
SGW (pH 7)	750 mg/L sodium chloride, 750 mg/L sodium bicarbonate	100°C, 10.3 MPa	Organics
SGW plus hydraulic fracturing fluid	See Table 2.2	100°C, 10.3 MPa	Organics

Table 2.2 Hydraulic fracturing fluid solution composition used for the pressurised leach test

Chemical	**Role in hydraulic fracturing**	**Concentration[a] (gallons or lbs/gallon#)**	**Concentration[b] (mg/L)**
Potassium carbonate	Buffer	2.5/1000	1500
Citric acid	Fe control	20 lbs/1000	2400
Acetic acid	Buffer/Fe control	20/1000	1500
Sodium hydroxide	Buffer	2/1000	1200
Ethanolamine	Crosslinker	2/1000	1200
2-bromo-2-nitro-1,3-propanediol	Biocide	0.15 lbs/1000	18
Sodium hydroxide	Biocide mixture (BE-7$^{\text{TM}}$)	3/1000	60
Sodium hypochlorite			600
Polyacrylate	Scale inhibitor	0.5/1000	300
Isopropanol	Surfactant mixture (GasPerm$^{\text{TM}}$ 1100)	10/1000	1000
Methanol			1000
Ethanol			3000
Sweet orange oil			500
Ethylene glycol monobutyl ether	Surfactant	5/1000	3000
Sodium thiosulfate	Gel stabilizer	3/1000	1800
Sodium persulfate	Breaker	2 lbs/1000	240
Potassium chloride	Clay control	0.25 lbs/1000	30
Tetramethylammonium chloride	Clay control	35/1000	35 000
Ammonium sulfate	Friction reducer	2/1000	600
Sodium bicarbonate	Groundwater[c]	-	750
Sodium chloride	Groundwater	-	750

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[a] based on information from: Halliburton (2014). [b] final pH of solution adjusted to pH 7.5 with glacial acetic acid equating to approximately 0.8 mg/L. [c] based on 1500 mg/L total dissolved solids (TDS), composed of 750 mg/L $NaHCO_3$ and 750 mg/L NaCl; median value reported in Worley Parsons (2010) Spatial Analysis of Coal Seam Water Chemistry for Department of Environment and Resource Management (DERM), Queensland. [#] 1 US gallon = 3.785 L; 1 lb = 0.454 kg.

2.2 Sample collection and preparation

Preliminary test work carried out to optimise the leach tests conducted for trace element and radionuclide studies was conducted on a coal sample sourced from the CSIRO Energy Technology's coal archive at Lucas Heights. The sample, from the German Creek coal mine (located in the Bowen Basin, Queensland) was approximately 10 years old and had been stored in a sealed polythene bag after drying and crushing. The sample was deemed fit for purpose as the sole objective of the experimental work was to optimise the leach test conditions for constituents that would not be prone to losses through volatilisation. It should be noted, however, that some pyrite oxidation may have occurred during prolonged storage which may have resulted in increased mobility of some trace elements.

Coal samples for the main study were sourced through CSIRO Energy Technology’s Coal Preparation Group at Pinjarra Hills, Queensland. The group receives coal samples for process-related work from various coal mines across Australia. Eight coal samples were subsequently selected for use in the study, which originated from a number of coal basins across Australia (Table 2.3). Wherever possible, coal samples that were selected for use were less than 12 months old (from the date of collection) and had been stored as received in sealed metal drums.

The coal samples (0.5 to 1 kg) were provided in a variety of sizes ranging from discrete core sections to coarse powders. All samples were subsequently air dried, crushed with the aid of a mallet, ground with an electric grinder and passed through a polypropylene mesh sieve (2 mm diameter mesh). The prepared samples were then refrigerated in sealed containers until required for the experimental studies. The sample preparation steps were designed to minimise loss of volatile coal components; however, losses of volatile organic compounds (benzene, toluene, ethylbenzene, and xylenes [BTEX]) during the air drying step cannot be discounted. Therefore, BTEX were not included in the present study. Total trace element concentrations were determined on sub-samples of each coal sample.

The ash content of the dried coal samples was determined gravimetrically. Pre-weighed sub-samples of each coal type were placed in covered silica trays and gradually heated to 550^{o}C and maintained at the temperature for a period of 8 hours in order to volatilise the organic components. The sub-samples were then cooled to room temperature in a desiccator and reweighed. Ash contents are reported in Table 2.4.

Table 2.3 Details of the coal samples used in the study

Name of sample	Coal basin	Location	Coal size	Storage	Approximate date of sample collection
Wandoan 2009	Surat	Western Darling Downs, Qld, 60 km south of Taroom	Moist, coarse grind, <2 mm	Plastic bag in laboratory	October 2009
Wandoan 2011	Surat	Not specified	Coarse lumps	Stored wet	2011
Blackwater	Bowen	Stewarton, Central Qld	Coarse grind, <~5 mm	Stored wet for 3 months	2013
Oaky Creek	Bowen	Bowen Basin between Middlemount and Tieri, Qld	<2 mm	Stored wet	Mid 2013
Carsborough Downs	Bowen	Near Moranbah in the northern Bowen Basin, Qld	<2 mm	Stored wet	2013
Galilee	Galilee	Not specified	Bore core segments	As a moist core in a plastic bag	Early 2013
Narrabri	Gunnedah	28 km south of Narrabri, NSW	<2 mm	Stored wet	Nov 2013
New Acland	Surat	About 10 km north of Oakey (Darling Downs), Qld	Wet lumps of coal	Plastic bag	Nov 2013

Table 2.4 Ash content of the coal samples used in the study

Name of sample	Coal basin	Ash content (%)
Wandoan 2009	Surat	8.4
Wandoan 2011	Surat	9.7
Blackwater	Bowen	9.0
Oaky Creek	Bowen	7.8
Carsborough Downs	Bowen	7.9
Galilee	Galilee	14.0
Narrabri	Gunnedah	9.8
New Acland	Surat	55.0

2.3 Leach test protocols

2.3.1 Trace elements and radionuclides

A series of preliminary experiments were carried out using the German Creek coal sample to optimise the leaching protocols used in subsequent analyses. The objective of this step was to characterise how the key experimental parameters affected trace element release and select routine operating conditions that would yield reproducible results. Sub-samples of this coal sample were leached with 0.01 M hydrochloric acid solution. A range of leaching temperatures (24, 40, 67 and 75°C) were trialed, as well as varying solids concentrations (10, 50 and 200 g/L), mixing durations (2, 18 and 42 h) and two mixing methods (shaker and bottle roller). Samples were prepared in polypropylene centrifuge tubes and were mixed over the time course of the leach test using either a commercially-available incubator shaker (IKA Malaysia, KS 4000 i control) set at a mixing speed control setting of 60 rpm or a purpose-built bottle roller set at 60 rpm. Following mixing for specified periods (see ensuing text for further details), the coal suspensions were centrifuged at 3000 rpm for three minutes, and then syringe filtered through 0.45 μm filter cartridges (Minisart, Sartorius Stedim, Germany) prior to trace element analysis.

Following optimisation of the experimental method, leach tests were carried out on each coal sample using four different leaching solutions. The composition of each leach solution is presented previously in Table 2.1. All reagents used in the preparation of the leach solutions were of analytical grade or higher.

Leaching experiments were undertaken by weighing a known mass of coal sample into 50 mL polypropylene centrifuge tubes, along with the required volume of leach solution to achieve the desired solids concentration (e.g. for a solids concentration of 200 g/L, 9 g of coal was mixed with 45 mL of leach solution).

The centrifuge tubes were capped, shaken and then placed horizontally in an incubator shaker (IKA Malaysia, KS 4000 i control,) capable of temperature and mixing speed control, and left to mix. Each coal sample underwent each leach test in triplicate. For quality assurance and quality control purposes, three blank leach solutions were carried through the entire process for each leach test.

The purpose of the dilute hydrochloric acid leach test was to equilibrate the coal samples in an acidic environment (pH 1.5 to 2) under which conditions there would be some mineral dissolution and release of trace element into solution. The amount of acid required to achieve this pH range was first assessed by titration of coal sub-samples with dilute acid. For most samples the desired pH range was achieved by using a 0.1 M hydrochloric acid solution. However, the Narrabri sample had a significant buffering capacity (most likely associated with high carbonate content) and required a 0.2 M hydrochloric acid solution to achieve the desired pH.

Following mixing for specified time periods, the coal suspensions were centrifuged at 3000 rpm for three minutes, and then syringe filtered through 0.45 μm filter cartridges (Minisart, Sartorius Stedim, Germany). Sub-samples for fluoride, sulfate and chloride were collected and kept refrigerated, while sub-samples for trace elements were acidified to contain 2% v/v nitric acid (Merck Tracepur).

Samples for radiochemical analysis required larger amounts of sample (100 mL). The same procedure was used, but three separate extracts were carried out and they were combined after filtering. The extracts were then acidified to pH 2 with nitric acid (Merck Tracepur).

2.4 Analytical procedures – trace elements and radionuclides

Trace element analysis was carried out at CSIRO using both inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian 730-ES, Australia) and ICP-MS (7500CE, Agilent Technologies, Japan). Limits of detection were calculated as three times the standard deviation (3 Sigma) of the analytical blank measurements. The CSIRO laboratory is a National Association of Testing Authorities (NATA) accredited facility for trace element analysis.

The ICP-AES was calibrated with matrix matched (2% v/v nitric acid) standards (AccuStandard, US) for the analysis of the 0.01 M HCl leach solutions (which were acidified to 2% v/v nitric acid). Analysis of the other leach solutions (Table 2.1) was carried out using the method of standard additions to overcome analyte suppression caused by the high concentrations of total dissolved solids (TDS).

The ICP-MS was calibrated with certified reference standards (QCD Analysts) prepared in a mix of 2.25% v/v nitric acid and 0.75% v/v hydrochloric acid. The dilute HCl leach solutions were diluted three-fold with de-ionised water such that the final acid concentrations matched that of the standards. To reduce analyte suppression induced by the other leach solution matrices, these leach solutions were diluted 50-fold with de-ionised water such that the final acid concentrations matched that of the standards.

Total elemental analysis was also undertaken on the solid coal samples. Coal samples were digested using a pressurised nitric acid, microwave-digestion method based on that of Wang et al. (2006). In brief, 50 mg of sample was mixed with 10 mL of concentrated nitric acid (Merck, Tracepur) and heated in a commercial microwave oven (MARS Xpress, CEM). Digests were diluted with ultra-pure water (Milli-Q, 18 MΩ/cm) and analysed by ICP-AES and ICP-MS using matrix matched standards. The coal certified reference material SARM-18 (South African Bureau of Standards) was also analysed as a check on accuracy.

The analysis of inorganic anions (chloride, sulfate and fluoride) was carried out on sub-samples of the leachates. Analyses were performed by the National Measurement Institute (NMI), Sydney, using their standard ion chromatographic methods. NMI is a NATA accredited laboratory.

Radium-226 analysis was conducted on selected leachate and coal samples by the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, NSW, using their standard analytical methods. Ra-226 was measured in the leachates by a method based on United States Environmental Protection Agency (US EPA) procedure 9315 (US EPA 1986). This involved chemical separation of radium as a precipitate of radium sulfate. The precipitate was measured selectively by alpha spectrometry. For radionuclide determination in the solid coal samples, milled coal was packed and sealed in Petri dishes, left to equilibrate for three weeks and measured by Compton suppression gamma spectrometry. Total uranium and thorium concentrations in leach samples and solid coal digests were quantified by ICP-MS at CSIRO (see above). Total activities for uranium and thorium in leachate samples were estimated by calculation from the ICP-MS data using specific activities derived assuming that uranium and thorium are present in their natural isotopic abundance in environmental samples (IEM 2014). The specific activity values used in these calculations were 0.0263 and 0.0081 Bq/µg for uranium and thorium respectively.

2.5 Organic contaminants

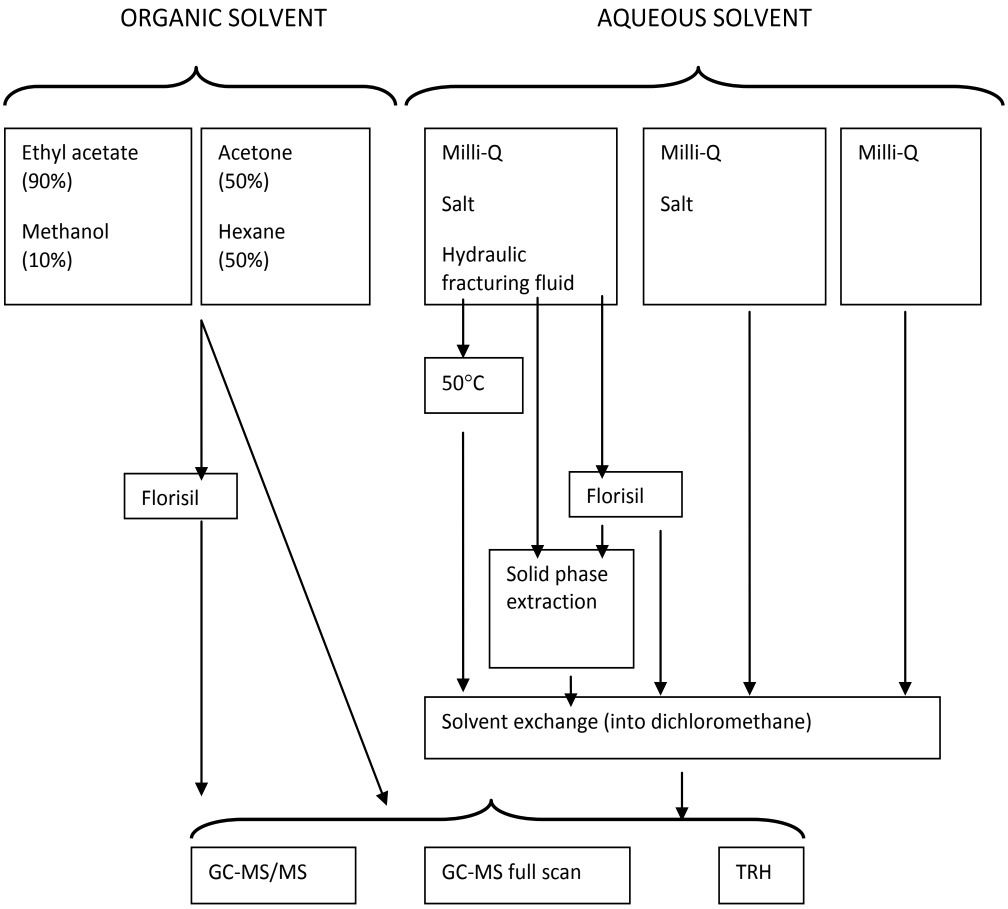
2.5.1 Testing and optimisation of the organic analysis methods

Unlike inorganic geogenic contaminants, the analytical methods for geogenic organic compounds are not yet fully developed. Therefore, the primary aim of the studies on organic substances was to test and optimise analytical methods and compare the leaching ability of different leachates including hydraulic fracturing fluid.

Coal is a highly complex macromolecular structure comprising a vast array of organic compounds with a correspondingly large diversity in their characteristics (Orem & Finkelman 2003; Radke et al. 1980; Stout & Emsbo-Mattingly 2008). It is therefore a considerable challenge to select representative geogenic organic compounds in coal for quantitative analysis. To overcome this problem, the selection of organic compounds for quantitative analysis was based on their previous identification in coals, that were leached with a range of organic and aqueous solvents (Achten & Hoffman 2009; Misz-Kennan & Fabianska 2011; Skret et al. 2010), or produced waters from coal seam gas activity (Orem et al. 2007; Pashin et al. 2013), and are summarised in Appendix C (Table C.1). Because of the number of different organic compounds present in coal, non-target analysis of leached organic compounds was also undertaken through searching established mass spectrometry chemical libraries of organic compounds. Also, the total recoverable hydrocarbons (TRH) containing between 10 and 36 carbon atoms were measured in the leachates.

Prior to conducting the main leaching experiments, a preliminary assessment of the coal leaching was undertaken on the German Creek coal sample to assess a range of solvents and sample leaching procedures to optimise the methods for the coal samples. In general, hydrophobic geogenic organic compounds in coal are expected to be more amenable to leaching into hydrophobic solvents (Miranda et al. 1999; Wang et al. 2010), than in water-based or aqueous solvents. The leaching efficiency of two different mixtures of organic solvents was therefore investigated to gain additional insights into the release of organic compounds from coal. An overview of the methodology for the preliminary assessment is presented in Figure 2.1, including leaching solvents, leaching conditions and leachate clean-up steps. Leaching experiments were conducted with all coal samples listed in Table 2.3, with associated quantitative (gas chromatography-mass spectrometry (GC-MS)/MS) and non-targeted (GC-MS full scan and TRH) analysis.

The detection and quantification of organic compounds in coal leachates may be affected by two factors. First, due to the carbon-rich nature of coal the leaching efficiency may be low, especially for hydrophobic organic compounds (e.g. Braida et al. 2003; Cornelissen et al. 2005; Koelmans et al. 2006). Secondly, the presence of a diverse range of unidentifiable organic compounds present in coal could also leach out and cause interferences (Orem & Finkelman 2003; Orem et al. 2007; Rahman et al. 2013). This is generally known as matrix effect. These two factors were therefore assessed in both organic and aqueous solvent leachates. This was done by comparing the measured response of a number of organic compounds (Appendix C, Table C.1) from a matrix-free substrate (in this case, an acid-washed sand) and a spiked coal.



The standard conditions were high pressure (10.3 MPa) and temperature (100 °C) unless otherwise specified. Ultrapure water (Milli-Q) plus salt was used to represent groundwater. Florisil® is a trade name for magnesium silicate used for clean-up of chemical extracts.

Figure 2.1 Overview of the extraction and clean-up steps applied during the organics optimisation phase of the project

2.5.2 Leach test overview

The preliminary leach tests (Figure 2.1) were designed to optimise conditions for leaching organic compounds from coal in both organic and aqueous solutions. This was to determine:

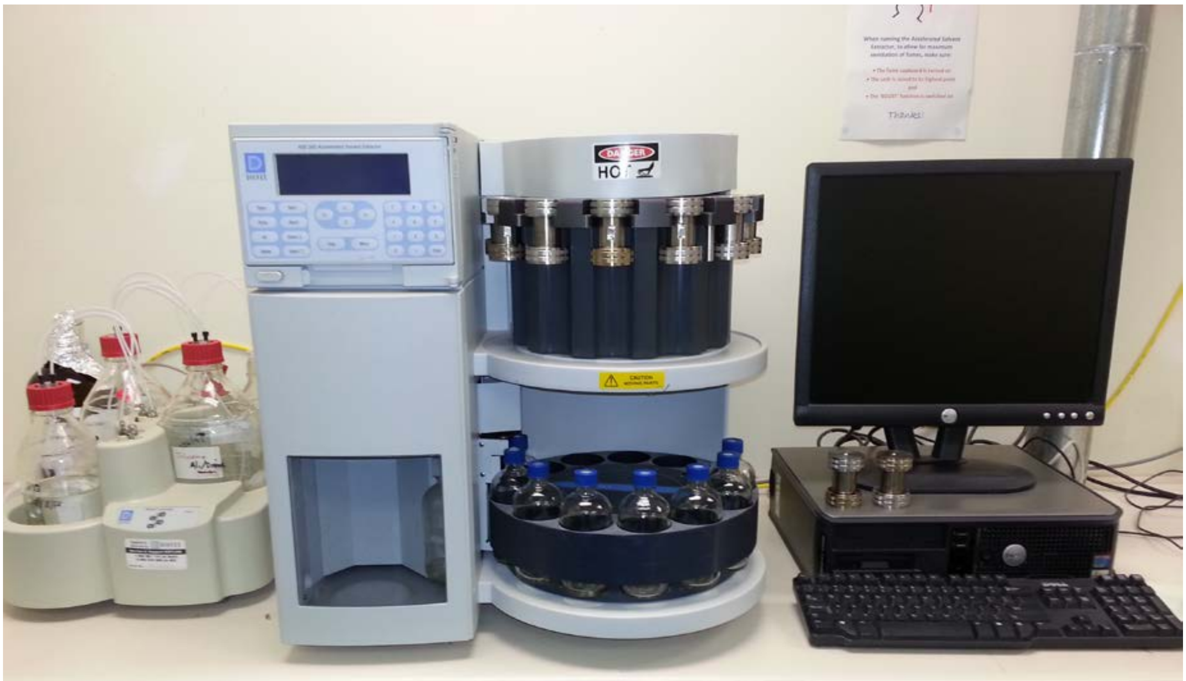
- the maximum amount of organic compounds that could be leached from coal, using an organic solvent
- the comparative amount that may be leached into aqueous solutions designed to be representative of groundwater and groundwater mixed with a solution containing chemicals that have been listed as being present in hydraulic fracturing fluids under Australian conditions (Table 2.2).

The SGW was composed of sodium chloride ($NaCl$) and sodium bicarbonate ($NaHCO_3$) at respective concentrations of 750 mg/L, to give a total TDS of 1500 mg/L and pH of 7.5. This composition has previously been identified as being the median for groundwater associated with coal seam regions (Worley Parsons 2010) as they are usually dominated by Na^+, Cl^- and HCO_3^- ions. The consideration of a salt solution in contact with the coal was important since it has been observed that the water solubility of organic compounds can be influenced by the presence of ions in solution (e.g. Gorgenyi et al. 2006; Patel et al. 2003). In combination with the chemicals listed in Table 2.2, this SGW was designed to represent the combination of the hydraulic fracturing fluid injected into a coal seam with water present in the coal seam.

Following the initial investigations, the main set of leach tests were conducted on the 8 coal samples described in Table 2.3. The leach tests were conducted at high temperature and pressure using an accelerated solvent extraction (ASE) apparatus (Figure 2.2 below) with SGW and SGW amended with the in-house prepared hydraulic fracturing fluid (Table 2.2) as the leaching solutions.

2.5.3 Leach test procedure

To apply certain temperature and pressure conditions during leach tests, a Dionex ASE system was used. Following the methods recommended by the manufacturer, coal was weighed into 1 g aliquots, mixed with approximately 18 g of acid-washed sand (representing an inert matrix free of organic carbon) and added to a stainless-steel cell. Sand, without coal, was also used as a blank control (addition of acetone only) and spiked control (addition of organic compounds in acetone). All leaching experiments were conducted at 10.3 MPa (1500 psi) and 100°C for a time period of 20 minutes using the ASE system (Figure 2.2), with the exception of a 50°C treatment (also leached at 10.3 MPa) which was undertaken for organic solvent optimisation. Organic solvent mixtures selected for maximal leaching efficiency included a mixture of hexane and acetone (50:50) and ethyl acetate and methanol (90:10). The three different aqueous leachates were composed of the constituents shown in Figure 2.1.



Source: CSIRO. Photographer: Sheridan Martin. Note: the ASE can be programmed to different temperature and pressure combinations to enhance the recovery of organic compounds from difficult matrices.

Figure 2.2 The accelerated solvent extractor (ASE) unit used to extract the organic compounds from the carbon-rich coal matrix

Following the extraction phase, organic solvent leachates were evaporated to near-dryness and re-constituted in 1 mL of dichloromethane. Aqueous leachates were solvent-exchanged with 4 x 5 mL of dichloromethane, evaporated to dryness (preliminary study) or approximately 0.5 mL (main study) and re-constituted in 1 mL of dichloromethane. All samples were passed through dry sodium sulfate (Na_2SO_4) prior to analysis to remove residual water. Further clean-up steps included passing re-constituted dichloromethane solutions through pre-conditioned Florisil® (magnesium silicate) or Oasis hydrophilic-lipophilic balance (HLB) solid phase extraction (SPE) cartridges.

Spiked treatments, where 1 g coal samples and sand samples were spiked with 100 µL of 10 mg/L solution of organic compounds, were leached along with coal samples to assess the extent of recovery of compounds from both coal and sand.

Leachates were analysed for selected polycyclic aromatic hydrocarbons (PAHs) and phenols with GC-MS/MS (Appendix C, Table C.1) and for major total TRH fractions using GC techniques. Non-target organic compounds were analysed by GC-MS and were identified by matching their obtained mass spectra against standard spectra contained in an online library of mass spectra (US National Institute of Standards (NIST)).

2.6 Organic analysis procedures

For analysis of non-target compounds, 2 µL of leached samples were injected into an Agilent 6890 GC coupled with a 5973 MS. Separation of analytes in the GC was performed with an HP-5MS. 30 m x 0.25 mm column (0.25 µm film thickness), using helium as a carrier gas at a constant flow rate of 1.1 mL/min and the injector set at 230°C in pulsed, splitless mode. The initial oven temperature was 40°C held for 1 min, with a 15°C/min ramp up to 100°C, followed by 20°C/min ramp up to 240°C then a 5°C/min ramp up to a final temperature of 315°C (held for 7.5 min), giving a total run time of 35 min. The MS was set to full scan mode, covering a mass range of m/z 50-500 at a scan rate of 50 ms, using electron impact ionisation (-70 eV). Data from the GC-MS were analysed using the NIST/EPA/NIH mass spectral library (2002) within Agilent MSD Chemstation software (version D.02.00.275). Mass spectral data of all significant peaks (defined as approximately >3 times the signal to noise ratio of the baseline) were compared with mass spectral data stored in the NIST library, that contains mass spectra for more than 147 000 organic compounds. Any match of less than 50% of compared value (based on similarity of mass value and relative intensity) was treated as unreliable and was not included.

Analysis of selected organic compounds (e.g. PAHs and phenols) was undertaken following injection of 1 µL of leached samples into an Agilent 7960A GC coupled with an Agilent 7000A tandem mass spectrometer (MS/MS). Separation of analytes in the GC was performed with an HP-5MS 30 m x 0.25 mm (0.25 µm film thickness) column, using helium as a carrier gas at a constant flow rate of 1 mL/min and the injector set at 230°C in pulsed splitless mode. The initial oven temperature was 40°C held for 1 min, with a 15°C/min ramp up to 100°C, followed by 20°C/min ramp up to 240°C then 5°C/min ramp up to a final temperature of 315°C (held for 7.5 min), giving a total run time of 35 min. The MS/MS was set to selected ion monitoring (SIM) mode, with the m/z values summarised in Appendix C (Table C.1), using electron impact ionisation (-70 eV). Data collected was analysed using Agilent MassHunter Workstation software (vB.06.00). Details of the limit of reporting (LOR) for each compound are also given in Appendix C (Table C.1).

Total recoverable hydrocarbons analysis was undertaken at the NMI laboratories (North Ryde, Sydney), where major TRH fractions containing compounds composed of 10 to 14 carbon atoms (C_{10}-C_{14}), 15 to 28 carbon atoms (C_{15}-C_{28}) and 29 to 36 carbon atoms (C_{29}-C_{36}) were analysed. The ranking of these fractions corresponds with increasingly hydrophobic compounds with decreasing volatility as the number of carbon atoms increases. The LOR for each TRH fraction was 50 mg/kg. Additional confirmatory analyses of phenol, monomethylphenols and dimethylphenols in the coal sample leachates were also undertaken by NMI, using their in-house standard methods.

3 Results

3.1 Optimisation of leach test protocols – trace elements

The effect of varying key leach test parameters (e.g. temperature, solids concentration, time, shaker type) on the leaching of various trace metals from the German Creek coal sample are summarised graphically in Appendix A.

Dissolved trace element concentrations generally increased with increasing temperature (24 to 75ºC). The exceptions to this trend were calcium, cadmium, copper, lead, phosphorus and strontium, where no temperature dependency was observed (Appendix A).

Increasing the solids concentration over the range 10 to 200 g/L also resulted in increasing dissolved trace element concentrations measured in the leach solutions (Appendix A). In most cases dissolved trace element concentrations varied linearly with solids concentration.

The effect of leach test duration (2, 18 and 42 hr) on dissolved trace element concentrations is shown in Appendix A. In most cases, trace element concentrations attained a plateau value after 18 hr. The concentrations measured at the maximum leach test duration of 42 hr were not appreciably different.

The effect of the type of mixing applied during the leach tests on dissolved trace element concentrations is shown in Appendix A. In general, the shaker mixer and horizontal roller treatments gave comparable values. Lower trace element concentrations were generally observed for the vortex mixer-vertical alignment indicating that this configuration afforded the least effective mixing of coal particles with the leach solution. For mainly practical reasons, the vortex mixer-horizontal alignment was selected as the best mixing approach for use in the optimised leach test protocol.

Based on the results described above, the optimised leach test parameters were:

- 200 g/L solids concentration
- 18 hr leach time
- vortex mixer with tubes placed horizontally.

A final leach test temperature of 40°C was chosen as this was within the range expected at depth within typical coal seams subject to coal seam gas extraction.

3.2 Trace element concentrations in the coal samples

The concentrations of sixty-one trace elements in the various coal samples are summarised in Table 4.1. These data are reported as a previous review of geogenic contaminants associated with coals (Apte et al. 2017) revealed a paucity of information in the open literature on the concentrations of trace elements in Australian coals. Analysis data for the Certified Reference Material coal sample SARM-18 are shown in Appendix B (Table B.1) and confirm acceptable accuracy for the certified elements.

The concentrations of many trace elements were quite variable and typically ranged by up to one order of magnitude across the coal samples (Table 3.1). The New Acland coal sample had the highest concentration of a number of trace elements including arsenic, cadmium, copper, iron, lead, manganese, thorium, uranium and zinc. This most likely is a consequence of the very high inorganic ash content, which was by far the highest of all of the samples collected (Table 2.4). Comparisons of the trace elemental data with the mean global crustal abundance values (Taylor 1964) shown in Table 3.1 indicated that only arsenic, bismuth, boron, selenium and lead had concentrations close to, or above these benchmark values. This comparison indicates that the coal samples were not particularly enriched in trace elements relative to global averages.

Statistical analysis indicated a number of statistically significant correlations between various trace elements but failed to reveal associations between trace elements that were useful in terms of gaining an insight into the processes of trace metal release into solution.

Table 3.1 Trace element concentrations (mg/kg) in the coal samples

Sample description	Wandoan 2009	Wandoan 2011	Blackwater	Oaky Creek	Carsborough Downs	Galilee Basin	Narrabri	New Acland	Limit of detection	Mean crustal abundance
Al	14 000	13 000	7500	13 000	11 000	9200	11 000	67 000	***200***	***82 300***
Sb	0.01	0.04	0.05	0.04	**0.22**	0.03	0.04	0.01	***0.004***	***0.2***
As	1.7	1.3	0.5	1.3	1.2	1.3	1.6	**2.5**	***0.2***	***1.8***
Ba	160	140	18	41	10	19	41	90	***0.2***	***425***
Be	0.96	0.58	0.44	1.06	0.45	0.7	0.56	1.08	***0.005***	***2.8***
Bi	0.1	0.08	0.11	**0.2**	0.14	**0.18**	0.17	**0.28**	***0.004***	***0.17***
B	**26**	**23**	6	**16**	1.7	**27**	**13**	**17**	***0.4***	***10***
Cd	0.07	0.03	0.04	0.09	0.08	0.03	0.1	0.18	***0.01***	***0.2***
Cs	0.38	0.19	0.14	0.67	0.26	0.09	0.22	0.97	***0.03***	***3***
Ca	4600	3600	1200	1300	2000	1300	3400	1400	***4***	***41 500***
Ce	10	9	11	16	16	17	14	43	***0.1***	***60***
Cr	4.4	1.7	3.4	3.4	9.4	3.5	5.7	6.6	***0.2***	***100***
Co	4.5	3.7	2.1	2.5	3.3	4.5	1.4	3.7	***0.005***	***25***
Cu	8.1	6.5	10	17	16	7	8.9	25	***0.03***	***55***
Dy	1.5	1.3	0.81	1.67	1.27	1.21	1.07	**3.22**	***0.005***	***3***
Er	0.95	0.78	0.44	1.01	0.63	0.66	0.56	1.64	***0.005***	***2.8***
Eu	0.41	0.37	0.23	0.4	0.37	0.35	0.26	1.01	***0.001***	***1.2***
Gd	1.54	1.4	1.01	1.9	1.54	1.56	1.29	4.23	***0.004***	***5.4***
Ga	4.5	3.5	2.6	4.5	3.3	3.5	3.9	**16**	***0.02***	***15***

Sample description	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**	**Limit of detection**	**Mean crustal abundance**
Hf	1.37	1.2	0.32	1.59	0.62	0.78	0.7	2.7	***0.01***	***3***
Ho	0.3	0.25	0.15	0.32	0.22	0.23	0.19	0.55	***0.002***	***1.2***
In	0.02	0.02	0.01	0.03	0.02	0.02	0.03	0.06	***0.003***	***0.1***
Ir	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	***0.03***	***-***
Fe	1800	1200	4600	2900	3500	6600	4000	14 000	***6***	***56 300***
La	4.5	4.2	4.5	7.2	7.2	7.6	6.7	20	***0.05***	***30***
Pb	9.5	4.8	2.9	5.4	6.1	4.3	4.4	16	***0.1***	***12.5***
Li	5.1	4.3	8.9	**27**	**28**	3.9	3.2	15	***0.04***	***20***
Lu	0.14	0.12	0.05	0.14	0.06	0.09	0.07	0.2	***0.002***	***0.5***
Mg	1200	1100	640	420	510	190	1500	2700	***6***	***23 300***
Mn	16	7.5	25	32	7.4	200	170	360	***0.2***	***950***
Mo	0.77	0.48	0.08	0.64	0.51	0.91	0.71	0.55	***0.01***	***1.5***
Nd	6	5.5	4.9	8.3	7.2	7.6	6.3	21	***0.04***	***28***
Ni	4	2.2	3.8	2	6	4.3	4.3	2.9	***0.2***	***75***
Nb	0.31	0.79	0.19	1.37	0.35	0.99	1.18	0.04	***0.03***	***20***
Os	<0.01	<0.01	0.02	0.01	0.02	0.01	<0.01	0.02	***0.01***	***-***
P	36	24	460	580	380	120	32	96	***20***	***1050***
Pt	0.01	0.01	<0.005	0.02	0.01	0.01	0.01	0.03	***0.005***	***-***
K	290	120	640	580	220	39	140	950	***8***	***20 900***
Rh	0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	***0.01***	***-***

Sample description	Wandoan 2009	Wandoan 2011	Blackwater	Oaky Creek	Carsborough Downs	Galilee Basin	Narrabri	New Acland	Limit of detection	Mean crustal abundance
Rb	1.8	0.8	2.9	3.2	1.8	0.5	1.2	4.7	***0.1***	***90***
Ru	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	***0.01***	***-***
Sm	1.46	1.29	1.07	1.85	1.58	1.58	1.32	4.38	***0.003***	***6***
Sc	4.4	3.7	2.4	3.5	2.7	3.3	2.4	9	***0.02***	***22***
Se	**0.29**	**0.36**	**0.29**	**0.99**	**0.34**	**0.88**	**1.2**	**0.58**	***0.01***	***0.05***
Ag	0.05	0.04	0.02	0.05	0.03	0.03	0.03	**0.08**	***0.02***	***0.07***
Sr	230	170	50	120	45	18	57	71	***0.2***	***375***
S	**2700**	**2100**	**3600**	**5700**	**2600**	**3300**	**3400**	**2900**	***70***	***260***
Ta	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	***0.01***	***2***
Te	0.04	0.04	0.04	0.06	0.03	0.06	0.05	0.05	***0.01***	***-***
Tb	0.23	0.2	0.13	0.26	0.21	0.2	0.17	0.54	***0.001***	***0.9***
Tl	0.1	0.08	0.04	0.09	0.02	0.14	0.09	0.17	***0.01***	***0.45***
Th	2.14	1.72	1.47	2.16	2.14	2.05	1.86	5.51	***0.02***	***9.6***
Tm	0.13	0.11	0.06	0.14	0.08	0.09	0.07	0.21	***0.0003***	***0.48***
Sn	0.72	0.31	0.21	0.43	1.42	0.41	0.69	1.28	***0.05***	***2***
Ti	760	670	190	450	270	500	430	1200	***8***	***5700***
W	<0.01	0.04	0.03	0.04	0.03	0.16	0.02	0.02	***0.01***	***1.5***
U	0.59	0.43	0.23	0.68	0.34	0.55	0.37	1.1	***0.002***	***2.7***
V	28	18	13	42	20	22	15	44	***0.1***	***135***
Yb	0.98	0.83	0.37	0.99	0.5	0.62	0.49	1.44	***0.0003***	***3***

Sample description	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**	**Limit of detection**	**Mean crustal abundance**
Zn	11	4.4	5.6	16	8.2	6.6	6.9	25	***0.2***	***70***
Zr	53	46	11	69	24	31	31	120	***0.3***	***165***

Note. Concentrations exceeding the mean crustal abundance are marked in ***bold****.*

3.3 Leach test results – trace elements

Following optimisation, leach tests were carried out as planned on the eight coal samples using the following extractants:

- dilute hydrochloric acid (0.1 or 0.2 M – Narrabri coal sample only)
- pH 5 buffer with citrate added
- pH 7 buffer
- pH 7 buffer with citrate added.

Raw data (triplicate measurements and blank data) for all leach tests are reported in the supplementary data appendix (available at https://data.csiro.au). Average final pH data for the leachate samples is summarised in Table 3.2.

In order to assess the environmental significance of the leach test data, trace element leachate concentrations were compared with the available Australia and New Zealand water quality guidelines for aquatic ecosystem protection (ANZECC and ARMCANZ 2000) (Table 3.3). Depending on a number of factors, the guideline values are classified as high, moderate, and low reliability. For several metals, the guidelines also provide a number of values which correspond to different levels of ecosystem protection. Wherever possible, the 95% protection guideline value was used as the preferred benchmark as it is intended for application to moderately disturbed ecosystems. Of the 25 available guideline values, 13 were high reliability values for 95% species protection. The values for antimony, cobalt, thallium, uranium and vanadium were low reliability, whereas the manganese value was medium reliability and the molybdenum, gallium, bismuth, beryllium, lanthanum and thallium guidelines were environmental concern levels (lowest reliability). For further details on the derivation and significance of these guideline values see ANZECC and ARMCANZ (2000). The ANZECC and ARMCANZ low reliability environmental concern level for lanthanum of 0.04 µg/L was not used in this assessment as the value is below typical background concentrations in many uncontaminated natural waters and therefore is of little practical value.

It is noted that no toxicology-based water quality guideline values exist for the less common elements and it is therefore difficult to interpret the leachate concentration data in terms of potential environmental risk. A review of international water quality guidelines for aquatic ecosystem protection was conducted as part of this study and no relevant guidelines for elements not already covered by the ANZECC and ARMCANZ (2000) guidelines were found.

Table 3.2 Final pH values observed during the leach tests

Sample description	Dilute HCl	pH 5 citrate	pH 7 citrate	pH 7 no citrate
Wandoan 2009	1.73	5.4	7.1	7.1
Wandoan 2011	1.65	5.7	7.4	7.5
Blackwater	1.62	5.9	8.3	8.1
Oaky Creek	1.54	5.1	8.5	8.4
Carsborough Downs	1.62	6.5	8.5	8.4

Sample description	Dilute HCl	pH 5 citrate	pH 7 citrate	pH 7 no citrate
Galilee	1.76	5.7	7.6	7.5
Narrabri	1.70	5.9	8.4	8.2
New Acland	1.93	5.4	7.7	7.6

Table 3.3 ANZECC and ARMCANZ (2000) water quality guideline values used as benchmarks

Element	Guideline value (µg/L)	Comments
Ag	0.05	95% species protection level
Al	55	95% species protection level
As	13	95% species protection level. Arsenic present as As(III)
B	370	95% species protection level
Be	0.13	95% species protection level
Bi	0.7	Low reliability: environmental concern level
Cd	0.2	95% species protection level
Co	1.4	Low reliability
Cr	1	Chromium present as Cr(VI), 95% species protection level
Cu	1.4	95% species protection level
Ga	18	Low reliability: environmental concern level
Hg	0.6	95% species protection level
La	0.04	Low reliability: environmental concern level
Mn	1700	Medium reliability
Mo	34	Low reliability: environmental concern level
Ni	11	95% species protection level
Pb	3.4	95% species protection level
Sb	9	95%, Low reliability
Se	5	95% species protection level
Sn	3	Low reliability
Tl	0.03	Low reliability
U	0.5	Low reliability
V	6	Low reliability
Zn	8	95% species protection level

3.4 Acid-extractable metals

Trace element concentrations measured in the dilute hydrochloric acid leachates of the eight coal samples are summarised in Table 3.4. Sixty-two trace elements were quantified. Given the aggressive nature of this leach test, the data give an indication of the upper bound estimates of the release of geogenic contaminants.

ICP-MS is a highly sensitive analytical technique capable of detecting many elements at sub--ppb concentrations and most of the 62 trace elements were detectable. Only mercury, iridium and osmium were below their respective detection limits (Appendix B, Table B.2) in all acid leachate samples. Trace element concentrations ranged from sub-µg/L (e.g. antimony, tin and silver) to mg/L (e.g. calcium, iron, magnesium and sodium). Similar to total element concentrations in the solid coal samples, there was a large variation in concentration between different coal types.

The following elements had one or more values above the chosen water quality benchmark values: aluminium, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, lead, manganese, nickel, selenium, silver, thallium, uranium, vanadium and zinc. These elements were therefore identified for further scrutiny.

Statistical analysis indicated a number of statistically significant correlations between various trace elements but failed to reveal associations between trace elements that were useful in terms of gaining an insight into the processes of trace metal release into solution.

Table 3.4 Dissolved trace element concentrations in dilute HCl leachates

	Units	**Guideline value**	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**
Al	mg/L	*0.055*	7.9	5.7	39	8.6	74	4.3	143	1.5
Sb	µg/L	*9*	0.03	0.01	0.19	0.71	1.51	<0.01	0.31	<0.01
As	µg/L	*13*	14	5.7	1.1	11	23	1	2.3	1.1
Ba	mg/L	-	3	5.7	0.4	0.7	0.5	1	2.5	0.5
Be	µg/L	*0.13*	5.8	4.2	6.4	13	11	8.3	2.53	8.6
B	µg/L	*370*	578	504	20	64	16	617	127	104
Cd	µg/L	*0.2*	1.8	1.3	0.6	1.4	0.7	1.4	4.4	33
Cs	µg/L	-	3.4	3.2	0.9	2.5	2.3	3.1	4.6	2.2
Ca	mg/L	-	365	241	226	152	405	109	527	94
Ce	µg/L	-	99	93	104	68	133	179	747	5
Bi	µg/L	-	0.1	0.04	0.78	1.82	1.82	0.03	0.6	<0.01
Cr	µg/L	*1*	4	0.7	31	3.3	134	3	43	0.4
Co	µg/L	*1.4*	35	18	4.9	16	24	27	23	36
Cu	µg/L	*1.4*	194	196	167	126	142	168	97	148
Dy	µg/L	-	6.5	4.2	45	42	97	20	38	0.9
Er	µg/L	-	3	1.9	21	22	42	10	19	0.4
Eu	µg/L	-	2.5	2.1	11	8.5	23	5.3	11	0.25
Gd	µg/L	-	9.3	6.6	50	41	106	24	53	1
Ga	µg/L	*18*	5.3	4.3	18	2.9	65	13	13	0.01

	Units	**Guideline value**	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**
Hf	µg/L	-	0.2	0.07	0.15	0.14	0.24	0.08	0.32	<0.01
Ho	µg/L	-	1.1	0.73	8.3	8.3	17.4	3.9	6.9	0.17
In	µg/L	-	0.36	0.25	0.65	0.46	1.1	0.31	0.6	0.2
Fe	mg/L	-	69	22	418	243	280	513	401	193
La	µg/L	*0.04*	40	39	25	16	28	80	368	2.1
Pb	µg/L	*3.4*	1648	232	141	89	251	262	304	117
Li	µg/L	-	32	27	92	97	224	15	19	25
Lu	µg/L	-	0.33	0.22	1.82	2.35	2.84	1.23	1.86	0.05
Mg	mg/L	-	49	56	61	33	41	17	215	109
Mn	mg/L	*1.7*	1.8	0.7	3.4	3.8	1.2	21	10	5.3
Mo	µg/L	*34*	0.18	0.03	0.49	4.1	6.4	0.14	0.68	0.06
Nd	µg/L	-	47	39	88	77	157	93	299	3.1
Ni	µg/L	*11*	11	1.9	18	20	35	11	35	8.9
Nb	µg/L	-	0.028	0.01	0.018	0.01	0.003	0.004	0.07	<0.002
P	mg/L	-	0.5	0.1	65	53	48.7	6	0.04	0.01
K	mg/L	-	5.2	3.7	1.5	3.5	0.9	1.9	4.7	6
Rh	µg/L	-	0.19	0.15	0.04	0.06	0.04	0.03	<0.1	0.04
Rb	µg/L	-	30	23	4.3	13	4.5	21	24	16
Ru	µg/L	-	0.04	0.04	<0.01	0.01	<0.01	<0.01	0.02	0.01
Sm	µg/L	-	9.8	7.3	36	31	77	23	60	0.8

	Units	**Guideline value**	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**
Sc	µg/L	-	10	5.1	33	25	61	14	73	2.1
Se	µg/L	*5*	1.6	1.1	2.1	2.7	4.2	2	11	3.3
Ag	µg/L	*0.05*	0.12	0.06	<0.01	<0.01	<0.01	<0.01	<0.1	0.11
Na	mg/L	-	221	123	3.7	137	6.2	33	113	82
Sr	mg/L	-	9.1	7.1	2.3	3.6	2	1.1	4	2.3
S	mg/L	-	8.6	0.8	10	65	1.2	4.4	4.4	10
Ta	µg/L	-	0.004	0.002	0.038	0.026	0.045	0.004	0.02	<0.001
Te	µg/L	-	0.5	0.54	0.53	0.49	0.94	1.9	<1	0.57
Tb	µg/L	-	1.3	0.84	8.1	7	18	3.6	7.4	0.16
Tl	µg/L	*0.03*	3.2	3.2	0.05	0.23	0.08	4.2	3.4	0.73
Th	µg/L	-	2.3	1.4	9.6	17	12	0.98	22	0.04
Tm	µg/L	-	0.38	0.25	2.4	2.9	4.6	1.4	2.3	0.06
Sn	µg/L	*3*	0.19	0.01	0.14	0.05	0.17	<0.01	0.68	<0.01
Ti	µg/L	-	45	47	6.7	2.1	11	86	114	0.2
W	µg/L	-	0.033	0.014	0.096	0.342	0.222	0.047	0.1	<0.001
U	µg/L	*0.5*	3.3	2.1	9.2	18	11	4.6	5.7	0.52
V	µg/L	*6*	203	141	210	37	269	370	120	28.8
Yb	µg/L	-	2.3	1.6	13	17	23	8.7	13	0.35
Zn	µg/L	*8*	465	215	258	300	352	437	253	595
Zr	µg/L	-	2.8	0.93	0.22	2.8	0.14	0.16	22	0.1

3.4.1 Leachate tests conducted with buffers and citrate

Coal samples were extracted with pH buffered SGW solutions amended with citrate to establish likely concentrations that may be leached by groundwater or other water percolating through the coal seams (see Table 2.1 for details). Citrate was added as it is a common constituent of hydraulic fracturing fluids and is likely to increase the release of several trace metals through complexation and the formation of soluble metal-citrate complexes. Results are shown in Table 3.5, Table 3.6 and Table 3.7.

The concentrations of the following elements were below the limit of detection in the leach tests summarised below and are not discussed further:

- pH 5 (citrate added) leach test: chromium, gold, hafnium, iridium, indium, niobium, platinum, rhodium, ruthenium, tellurium
- pH 7 leach test (citrate added): arsenic, beryllium, bismuth, cadmium, chromium, europium, gold, hafnium, iridium, indium, lutetium, neodymium, niobium, osmium, platinum, rhodium, ruthenium, scandium, silver, tantalum, tellurium, terbium, thallium, thulium, tin, tungsten and zirconium
- pH 7 leach test (no citrate added): arsenic, beryllium, bismuth, cadmium, cerium, chromium, dysprosium, erbium, gadolinium, gold, hafnium, holmium, iridium, indium, lanthanum, lutetium, neodymium, niobium, platinum, rhodium, ruthenium, scandium, silver, tantalum, tellurium, terbium, thallium, thulium, tin, titanium and yttrium.

As found with the total element concentrations in the solid coal samples, there was a large variation in leaching behaviour between different coal types. Typical concentrations detected ranged from the sub-µg/L to mg/L. Some trace elements such as aluminium and sulfur displayed large variability between the different coal samples.

As expected, pH had a significant effect on trace element concentrations in leachates with many elements having higher concentrations at pH 5 compared to pH 7. The exceptions to this trend were: molybdenum, strontium and vanadium which had higher concentrations in the pH 7 leachates.

The addition of citrate to the pH 7 leach solution increased the leachate concentrations of the following elements: aluminium, barium, beryllium, cerium, cobalt, copper, dysprosium, erbium, europium, iron, lanthanum, manganese, neodymium, nickel, thorium, uranium, ytterbium, zinc and zirconium. The enhancement effect was particularly strong for aluminium and iron which are known to form strong complexes with citrate. It is assumed that the other elements listed above also interact with citrate in a similar manner and form charged complexes which are soluble.

Statistical analysis revealed some statistically significant correlations between elements. Most noteworthy were the correlations between uranium and sulfur which were significantly correlated in all of the leachate tests (r>0.97).

The trace elements exceeding the selected water quality guideline benchmarks in one or more of the eight coal samples tested were as follows:

- pH 5 plus citrate: aluminium, beryllium, boron, cadmium, cobalt, copper, selenium, silver, uranium, vanadium and zinc
- pH 7 plus citrate: aluminium, cobalt, copper, selenium, uranium and vanadium
- pH 7 no citrate added: aluminium, copper, selenium, uranium and vanadium.

In terms of impacts on water quality, these elements are therefore worthy of further scrutiny.

Table 3.5 Dissolved trace element concentrations in pH 5 citrate leachates

	Units	**Limit of detection**	**Guideline value**	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**
Al	µg/L	*2*	*55*	1300	360	510	270	600	450	2900	1400
Sb	µg/L	*0.1*	*9*	0.1	<0.1	0.2	0.3	2.2	0.1	0.1	0.2
As	µg/L	*1*	*13*	3	2	<1	1	4	<1	1	<1
Ba	µg/L	*0.2*	-	870	570	100	120	230	310	1100	140
Be	µg/L	*0.02*	*0.13*	0.13	0.06	0.19	0.81	0.71	0.06	0.21	0.24
Bi	µg/L	*0.04*	*0.7*	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.06	<0.04
B	µg/L	*2*	*370*	400	210	13	48	9	280	130	100
Cd	µg/L	*0.4*	*0.2*	<0.4	<0.4	<0.4	0.4	<0.4	<0.4	1.4	0.4
Cs	µg/L	*0.04*	-	1.3	0.84	0.27	0.71	0.71	1.6	2.7	1.5
Ca	mg/L	*0.2*	-	170	37	21	15	95	33	200	18
Ce	µg/L	*0.05*	-	1.6	1.1	0.23	0.66	1.3	0.26	19	<0.05
Co	µg/L	*0.1*	*1.4*	4	0.7	0.6	7	4	0.8	6	3
Cu	µg/L	*0.5*	*1.4*	3	2	30	17	45	0.5	1	5
Dy	µg/L	*0.02*	-	0.54	0.3	0.62	1.2	1.9	0.3	1.1	0.06
Er	µg/L	*0.01*	-	0.38	0.18	0.41	0.83	1.1	0.15	0.66	0.04
Eu	µg/L	*0.01*	-	0.26	0.18	0.1	0.15	0.29	0.08	0.46	0.04
Gd	µg/L	*0.02*	-	0.42	0.34	0.47	0.93	1.4	0.12	1.6	0.06
Ga	µg/L	*0.04*	*18*	0.23	0.14	0.07	0.1	0.11	0.31	0.05	0.07
Ho	µg/L	*0.1*	-	0.1	0.1	0.1	0.2	0.4	0.1	0.2	<0.1

	Units	Limit of detection	Guideline value	Wandoan 2009	Wandoan 2011	Blackwater	Oaky Creek	Carsborough Downs	Galilee Basin	Narrabri	New Acland
In	µg/L	*0.04*	-	<0.04	<0.04	<0.04	<0.04	0.13	<0.04	<0.04	<0.04
Fe	mg/L	*0.02*	-	6.6	1.3	8.2	7.7	5.2	5.3	2.4	4.8
La	µg/L	*0.01*	*0.04*	0.66	0.48	0.07	0.19	0.36	0.12	12	0.03
Pb	µg/L	*0.3*	*3.4*	1.4	0.3	<0.3	1.4	2.1	<0.3	1.1	1.2
Li	µg/L	*0.1*	-	23	13	5.3	76	11	8.9	6.3	17
Lu	µg/L	*0.01*	-	0.04	0.02	0.05	0.07	0.13	0.04	0.06	<0.01
Mg	mg/L	*0.1*	-	25	15	9.5	12	6	6.7	68	25
Mn	µg/L	*0.1*	*1700*	400	80	320	270	190	1100	900	150
Mo	µg/L	*0.1*	*34*	1.4	0.3	0.2	2.3	8.1	0.3	0.2	1.3
Nd	µg/L	*0.02*	-	1.2	0.72	0.31	1	1.5	0.27	7.9	0.08
Ni	µg/L	*0.5*	*11*	1.4	<0.5	2.6	7.3	7.5	0.6	8.1	0.6
Os	µg/L	*0.05*	-	<0.05	<0.05	0.2	0.1	<0.05	<0.05	<0.05	0.1
Pd	µg/L	*0.1*	-	2.7	0.8	0.3	0.5	0.5	0.3	1.7	0.3
P	µg/L	*1*	-	67	15	70	100	150	6	<1	2
K	mg/L	*0.03*	-	3.6	2.2	1	2.2	0.8	1.8	3.3	4.3
Rb	µg/L	*0.02*	-	16	10	1.4	4.8	2.1	14	20	8.4
Sm	µg/L	*0.1*	-	0.3	0.2	0.2	0.5	0.7	0.1	1.3	<0.1
Sc	µg/L	*2*	-	7	<2	6	<2	18	3	5	10
Se	µg/L	*0.1*	*5*	2.4	2.1	1.4	0.9	2.7	3.1	21	3.6
Ag	µg/L	*0.1*	*0.05*	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1

	Units	Limit of detection	Guideline value	Wandoan 2009	Wandoan 2011	Blackwater	Oaky Creek	Carsborough Downs	Galilee Basin	Narrabri	New Acland
Sr	mg/L	*0.1*	-	4.2	1.3	0.4	0.6	0.5	0.5	2	0.5
S	mg/L	*1*	-	47	4	23	308	5	45	26	47
Ta	µg/L	*0.02*	-	<0.02	<0.02	0.05	0.02	<0.02	0.05	0.04	<0.02
Tb	µg/L	*0.01*	-	0.08	0.05	0.1	0.18	0.27	0.03	0.23	<0.01
Tl	µg/L	*0.1*	*0.03*	0.1	<0.1	0.1	0.1	0.1	0.2	0.5	0.2
Th	µg/L	*0.01*	-	0.93	0.28	0.54	0.69	0.69	0.06	0.41	0.2
Tm	µg/L	*0.01*	-	0.05	0.04	0.06	0.11	0.14	0.03	0.09	<0.01
Sn	µg/L	*0.04*	-	0.19	0.08	0.17	0.13	0.29	0.16	0.25	0.18
Ti	µg/L	*0.1*	-	13	5	0.3	0.8	0.7	2	0.3	0.1
W	µg/L	*0.1*	-	0.1	0.1	<0.1	0.8	<0.1	0.1	<0.1	<0.1
U	µg/L	*0.01*	*0.5*	0.94	0.23	0.74	4.8	0.68	1.2	0.31	0.99
V	µg/L	*0.1*	*6*	8.3	2.8	<0.1	<0.1	0.4	<0.1	<0.1	<0.1
Yb	µg/L	*0.01*	-	0.41	0.21	0.39	0.65	0.9	0.27	0.44	0.07
Zn	µg/L	*0.1*	*8*	19	3.6	13	48	22	2.4	19	12
Zr	µg/L	*0.2*	-	7.8	2.6	2.2	3.3	2.8	1.3	3	2.3

Table 3.6 Dissolved trace element concentrations in pH 7 citrate leachates

	Units	Limit of detection	Guideline value	Wandoan 2009	Wandoan 2011	Blackwater	Oaky Creek	Carsborough Downs	Galilee Basin	Narrabri	New Acland
Al	µg/L	*2*	*55*	440	130	110	31	93	210	500	41
Sb	µg/L	*0.2*	*9*	<0.2	<0.2	<0.2	0.2	1.2	<0.2	<0.2	0.2
Ba	µg/L	*0.4*	-	220	130	28	120	56	96	125	67
B	µg/L	*2*	*370*	320	170	14	36	11	230	110	63
Cs	µg/L	*0.1*	-	0.5	0.4	0.1	0.6	0.3	0.9	0.8	0.8
Ca	mg/L	*0.3*	-	19	7.8	8.3	8.3	7.2	11	6.4	9.1
Ce	µg/L	*0.01*	-	0.47	0.18	0.08	0.01	0.03	0.09	0.44	0.14
Co	µg/L	*0.3*	*1.4*	1.2	0.3	<0.3	1.2	0.6	0.3	0.4	1.4
Cu	µg/L	*1*	*1.4*	1	1	10	1	11	<1	<1	6
Dy	µg/L	*0.03*	-	0.2	0.05	0.05	0.03	0.04	0.1	0.18	<0.03
Er	µg/L	*0.01*	-	0.15	0.04	0.05	0.02	0.03	0.08	0.18	0.02
Gd	µg/L	*0.03*	-	0.17	<0.03	0.07	<0.03	<0.03	0.06	0.18	<0.03
Ga	µg/L	*0.02*	*18*	0.05	0.05	0.05	0.06	0.23	0.07	0.31	<0.02
Fe	µg/L	*100*	-	1500	200	330	110	190	320	220	<100
La	µg/L	*0.01*	*0.04*	0.19	0.05	0.02	<0.01	<0.01	0.04	0.2	0.05
Pb	µg/L	*0.04*	*3.4*	1.5	0.5	0.2	0.3	1	0.2	0.7	1
Li	µg/L	*0.01*	-	16	10	3.8	63	6	6	7	11
Mg	mg/L	*0.2*	-	7.3	5.6	5.4	7.9	2.8	3	3.4	13
Mn	µg/L	*0.4*	*1700*	50	15	49	20	9	270	24	34

	Units	**Limit of detection**	**Guideline value**	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**
Mo	µg/L	*0.3*	*34*	2.9	0.8	1.1	2.9	12	3	10	12
Ni	µg/L	*1*	*11*	<1	<1	1	3	2	<1	1	<1
Pd	µg/L	*0.1*	-	0.4	0.1	0.1	0.2	0.1	0.1	0.1	0.1
P	µg/L	*3*	-	9	<3	6	<3	<3	<3	<3	3
K	mg/L	*0.1*	-	2	1.5	0.9	1.8	0.7	1.4	2.5	3.3
Rb	µg/L	*0.03*	-	7.2	5.9	1	3.8	1.1	10	11	6.1
Sm	µg/L	*0.04*	-	0.07	<0.04	<0.04	<0.04	<0.04	0.04	0.12	<0.04
Se	µg/L	*0.2*	*5*	2.8	2	1.5	1	2	3.3	25	3.6
Sr	µg/L	*0.03*	-	870	300	180	390	130	170	160	220
S	mg/L	*2*	-	44	4	24	260	6	40	27	44
Th	µg/L	*0.03*	-	0.21	0.04	0.04	<0.03	<0.03	<0.03	0.08	<0.03
Ti	µg/L	*0.2*	-	1.7	0.4	<0.2	<0.2	<0.2	<0.2	<0.2	0.5
U	µg/L	*0.01*	*0.5*	0.44	0.07	0.45	3.6	0.4	0.51	0.89	0.47
V	µg/L	*0.5*	*6*	13	8.7	2.4	<0.5	2.1	4.4	2.5	3.8
Yb	µg/L	*0.02*	-	0.21	0.04	0.03	0.02	0.06	0.11	0.13	<0.02
Zn	µg/L	*0.1*	*8*	4.9	1.8	1.8	5.2	3.1	0.9	1.9	4.7

Table 3.7 Dissolved trace element concentrations in pH 7 (no citrate) leachates

	Units	**Limit of detection**	**Guideline value**	**Wandoan 2009**	**Wandoan 2011**	**Blackwater**	**Oaky Creek**	**Carsborough Downs**	**Galilee Basin**	**Narrabri**	**New Acland**
Al	µg/L	*0.3*	*55*	4.3	2.5	6.5	8.9	17	0.6	120	3.3
Sb	µg/L	*0.1*	*9*	0.1	0.1	0.1	0.1	1.2	<0.1	0.1	0.1
Ba	µg/L	*4*	-	210	120	32	110	62	120	170	110
B	µg/L	*1*	*370*	360	160	10	32	6.2	230	100	70
Cs	µg/L	*0.02*	-	0.57	0.51	0.14	0.61	0.47	1	0.83	1.2
Ca	mg/L	*0.1*	-	17	5.5	7.9	7.8	5.7	10	5.2	9.4
Co	µg/L	*0.04*	*1.4*	0.47	0.12	0.04	0.69	0.09	0.06	0.12	1.1
Cu	µg/L	*0.1*	*1.4*	1	0.5	2.7	1.2	2.9	0.6	0.7	4.9
Eu	µg/L	*0.01*	-	0.05	0.02	0.01	0.02	0.02	0.02	0.04	0.02
Ga	µg/L	*0.03*	*18*	0.05	0.04	<0.03	0.04	0.25	<0.03	0.28	<0.03
Fe	µg/L	*0.5*	-	4.4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.5
Pb	µg/L	*0.1*	*3.4*	1.2	0.5	0.1	0.4	0.9	0.4	0.8	1.1
Li	µg/L	*0.03*	-	18	10	4	66	6	7	6	11
Mg	mg/L	*0.1*	-	7.4	4.2	5.2	7.7	2.5	2.9	3.1	14
Mn	µg/L	*0.1*	*1700*	22	4.4	22	10	2.6	130	5.1	32
Mo	µg/L	*0.2*	*34*	2.1	0.8	1.2	4.3	12	1.3	9.2	11
Ni	µg/L	*1*	*11*	<1	<1	<1	3	<1	<1	<1	1
Os	µg/L	*0.03*	-	0.03	0.2	0.06	0.09	0.47	0.26	0.18	0.11
Pd	µg/L	*0.1*	-	0.5	0.2	0.1	0.2	0.1	0.1	0.1	0.1

	Units	Limit of detection	Guideline value	Wandoan 2009	Wandoan 2011	Blackwater	Oaky Creek	Carsborough Downs	Galilee Basin	Narrabri	New Acland
P	µg/L	*2*	-	3	<2	2	<2	<2	<2	<2	<2
K	mg/L	*0.02*	-	2.1	1.5	0.9	1.8	0.6	1.4	2.5	3.4
Rb	µg/L	*0.05*	-	8.2	6.4	1.1	4.1	1.2	11	11	6.6
Se	µg/L	*1*	*5*	2	2	2	1	1	3	23	3
Sr	µg/L	*0.2*	-	850	280	200	410	140	190	170	240
S	mg/L	*0.5*	-	17	1.2	10	98	2	15	9.7	17
Th	µg/L	*0.01*	-	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
W	µg/L	*0.04*	-	<0.04	0.45	0.12	0.17	0.56	0.25	0.12	0.05
U	µg/L	*0.01*	*0.5*	0.07	0.01	0.28	3.5	0.44	0.02	0.12	0.14
V	µg/L	*1*	*6*	8	6	1	<1	2	1	2	3
Zn	µg/L	*0.2*	*8*	2	1	1	3	1	<0.2	1	3
Zr	µg/L	*0.2*	-	0.4	0.6	<0.2	<0.2	0.5	<0.2	0.2	<0.2

3.4.2 Radionuclides

Radionuclide activities of the solid coal samples, as measured by gamma ray spectrometry, are reported in Table 3.8. The measured activities varied within a factor of two for most coal samples and there were few discernible trends in the data. However, the New Acland sample had the highest activities for 8 out of the 11 radionuclides measured, which is consistent with this sample having by far the highest ash (mineral) content (Table 2.4). There are no specific regulatory limits or guideline values for radionuclides in coal that can be used as benchmark values.

Ra-226 activities in the leachate samples are shown in Table 3.9. Radium is known to occur in coal seams and is susceptible to leaching into groundwater (Apte et al. 2017). It is also of importance as its decay product is radon-222. The measured activities correlated poorly with the concentration of other trace elements with the exception of manganese (r=0.841). The measured activities were generally very low and close to the detection limit (<0.006 Bq/L). By comparison, the ANZECC and ARMCANZ (2000) limit for Ra-226 in livestock drinking water is 5 Bq/L and the World Health Organisation (WHO) guidance level for Ra-226 in drinking water is 1 Bq/L (WHO 2008).

The concentrations of uranium and thorium measured in the leachate tests are reported in Table 3.4 to Table 3.7. In general, these elements were present at low to sub-µg/L concentrations. The calculated total activities of uranium and thorium radionuclides (Bq/L) are shown in Table 3.10 and Table 3.11 respectively. The radioactivity associated with these elements is low. Overall, the results suggest that the coal samples do not appear to be a significant source of radionuclides which would potentially give rise to radioactive contamination of groundwater or flowback/produced water. However, this does not preclude the pre-concentration of radionuclides in precipitates forming in flowback and produced water ponds, gathering lines, or during water treatment (e.g. in micro-filtration and reverse osmosis filters).

Table 3.8 Radionuclide activities of the solid coal samples

Sample	**^{226}Ra**	**^{228}Ra**	**^{137}Cs**	**^{40}K**	**^{210}Pb**	**^{214}Pb**	**^{214}Bi**	**^{212}Bi**	**^{208}Tl**	**^{228}Th**	**^{238}U**
	(Bq/kg)										
Wandoan 2009	9.6	11.0	<0.4	149	34.4	8.4	10.9	9.7	15.5	9.7	14.2
Wandoan 2011	8.3	12.2	<0.6	138	23.2	7.2	9.4	<11.3	12.1	<11.3	<12.1
Blackwater	8.1	7.6	0.7	233	57.2	7.2	9.0	<17.5	17.3	<17.5	<24.5
Oaky Creek	12.8	10.0	<0.5	191	54.2	13.3	12.4	<9.7	17.5	<9.7	19.4
Carsborough Downs	9.9	12.2	<0.6	193	47.0	9.6	10.3	13.2	14.8	13.2	<17.7
Galilee Basin	10.6	5.4	<0.9	145	43.4	7.6	13.5	<13.2	<14	<13.2	<24.3
Narrabri	10.3	10.1	<0.7	173	58.7	10.0	10.7	13.5	18.8	13.5	18.7
New Acland	16.5	26.0	<0.4	137	40.1	16.3	16.7	23.4	27.0	23.4	26.0

Table 3.9 Radium-226 activities in coal leachates

Sample	^{226}Ra activity, (Bq/L)	
	HCl leachates	pH 7 citrate
Mean blank	<0.006	<0.006
Wandoan 2009	0.014 ± 0.002	<0.006
Wandoan 2011	0.019 ± 0.002	<0.006
Blackwater	0.013 ± 0.002	<0.006
Oaky Creek	<0.006	<0.006
Carsborough Downs	0.025 ± 0.003	<0.006
Galilee Basin	0.142 ± 0.012	0.019 ± 0.003
Narrabri	0.075 ± 0.006	0.020 ± 0.003
New Acland	0.016 ± 0.002	0.010 ± 0.002

Table 3.10 Total uranium activities in coal leachates

Sample	U activity, (Bq/L)	
	HCl leachates	pH 7 citrate
Wandoan 2009	0.087	0.012
Wandoan 2011	0.055	0.002
Blackwater	0.242	0.012
Oaky Creek	0.473	0.095
Carsborough Downs	0.289	0.011
Galilee Basin	0.121	0.013
Narrabri	0.150	0.023
New Acland	0.014	0.012

Table 3.11 Total thorium activities in coal leachates

Sample	**Th activity, (Bq/L)**	
	HCl leachates	**pH 7 citrate**
Wandoan 2009	0.0186	0.0017
Wandoan 2011	0.0113	0.0003
Blackwater	0.0778	0.0003
Oaky Creek	0.1377	<0.0001
Carsborough Downs	0.0972	<0.0001
Galilee Basin	0.0079	<0.0001
Narrabri	0.1782	0.0006
New Acland	0.0003	<0.0001

3.4.3 Major anions

The sulfate and fluoride concentrations measured during the leach tests are summarised in Table 3.12. The presence/absence of citrate had no effect on the concentration of either anion. Fluoride concentrations were in the low mg/L range and were highest in the acidic leachates. Sulfate concentrations were quite variable (range 1.5 to 210 mg/L) and were not related to pH of the leachate solutions. The Oaky Creek sample consistently leached the highest concentrations of sulfate.

Table 3.12 Major anion concentrations in coal leachates

Leach	**0.01 HCl**		**pH 5 citrate**		**pH 7 citrate**		**pH 7 no citrate**	
Sample description	**Sulfate**	**Fluoride**	**Sulfate**	**Fluoride**	**Sulfate**	**Fluoride**	**Sulfate**	**Fluoride**
	mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Limit of detection	***0.1***	***0.1***	***0.1***	***0.1***	***0.1***	***0.1***	***0.1***	***0.1***
Wandoan 2009	28	<0.1	33	<0.1	29	0.1	29	0.1
Wandoan 2011	2.1	<0.1	2.5	<0.1	1.7	0.1	1.5	0.1
Blackwater	13	2.6	12	0.1	14	0.2	14	0.2
Oaky Creek	190	3.6	210	0.2	180	0.3	190	0.4
Carsborough Downs	3.2	1.7	3.2	0.1	2.9	0.1	2.9	0.1
Galilee Basin	14	0.3	26	<0.1	26	0.2	24	0.2
Narrabri	14	0.2	16	0.3	16	0.8	16	0.8
New Acland	51	0.2	27	0.2	25	1.0	27	0.9

3.5 Optimisation of leach tests protocols - organics

3.5.1 Organic solvent extracts

Since the extraction with organic solvents represents the most effective means for releasing organic compounds from coal, it provides a likely upper bound estimate of matrix interferences (from co-eluted organic compounds) for the purposes of analytical method optimisation. Clean sand (inert matrix) was used as the control treatment. A marked matrix effect was noted on the apparent recovery of all organic compounds from coal in both of the organic solvent leachates (Appendix C, Table C.2, and Figure C.1). Generally, leaching of the test coal (German Creek sample) with organic solvents led to an overestimation of the amount of compound recovered (i.e. the recovery relative to the amount recovered from the control was >100%). The elevated response in the coal extracts suggests that the presence of other unidentified compounds concurrently leached from the coal matrix were also contributing to the measured signal of the organic compounds. To remove such interferences, clean-up of the extracts prior to their analysis was necessary. Tests showed that clean-up of extracts by passage through a Florisil® column significantly reduced the interferences in the solvent extract of the spiked coal, as it gave results that were closer to the control treatment. Nevertheless, the response of the cleaned-up leachate, remained much greater relative to the spiked sand control, indicating the complexity of organic solvent extracts of coals and the analytical challenges associated with coal as a matrix.

The concentrations of the organic compounds extracted by the hexane/acetone solvent mixture (with Florisil® clean-up) in the German Creek coal as a test sample are presented in Figure 3.1. The majority of the organic compounds that were detected were hydrophobic PAHs. Of the detectable compounds, the measured concentrations were in the low mg/L range. Apart from anthracene, dimethylphenols and fluorene, all of the detected compounds had between 15 and 28 carbon atoms. The fraction measured within this range (C_{15}-C_{28}) for the total recoverable hydrocarbons (TRH) analysis (Table 3.13) was substantially higher than the sum of the concentrations of the compounds presented in Figure 3.1. Also, organic solvents were comparatively ineffective at extracting lower molecular weight TRHs (C_{10}-C_{14}), which is highlighted in Table 3.13.

Table 3.13 Total recoverable hydrocarbons (TRH) in organic solvent and aqueous extracts of the test coal (German Creek sample)

Treatment	**TRH fraction (mg/L)**		
	C_{10}-C_{14}[a]	**C_{15}-C_{28}[b]**	**C_{29}-C_{36}[c]**
Organic solvents			
Hexane/acetone	<LOR[d]	940	380
Hexane/acetone (Florisil®)	<LOR	627	215
Ethyl acetate/methanol	<LOR	970	110
Ethyl acetate/methanol (Florisil®)	<LOR	730	280
Hydraulic fracturing fluid (HFF)			
SGW + HFF	85	<LOR	<LOR
SGW + HFF (Florisil®)	118	<LOR	<LOR
SGW + HFF (SPE)	111	<LOR	<LOR

[a] fraction containing compounds with 10 to 14 carbon atoms; [b] fraction containing compounds with 15 to 28 carbon atoms; [c] fraction containing compounds with 29 to 36 carbon atoms; [d]LOR is 50 mg/L

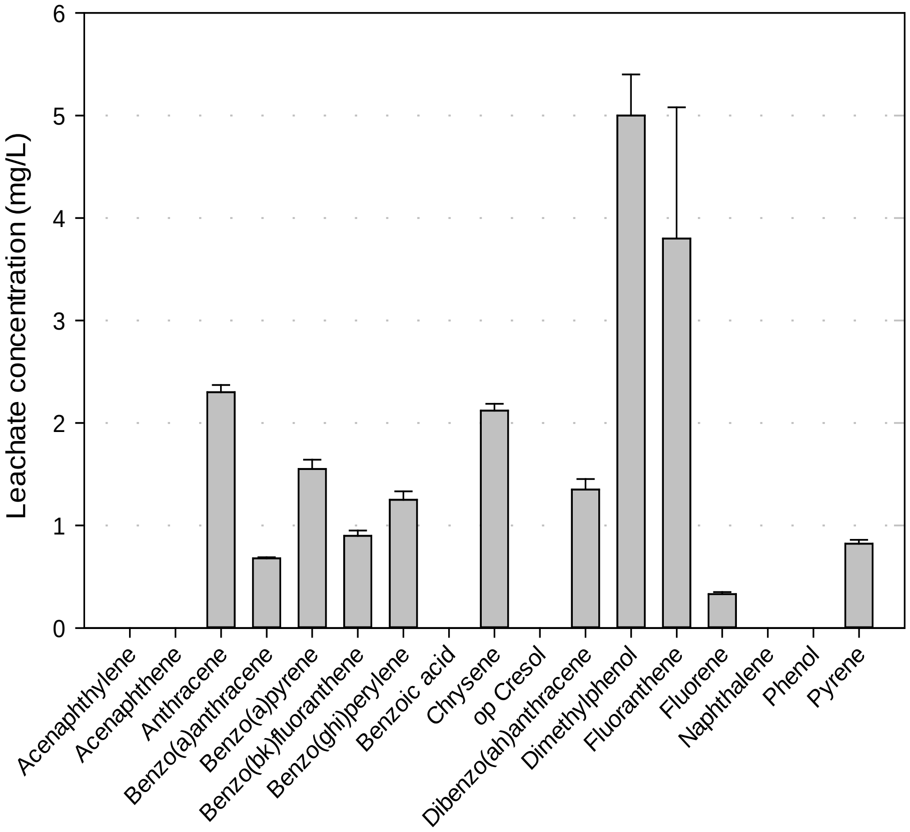


Figure 3.1 Concentrations of selected organic compounds in leachates from the German Creek test coal under standard conditions (10.3 MPa and 100°C) using hexane/acetone (50:50) with Florisil® clean-up during the method development

3.5.2 Aqueous extracts

In contrast to the organic solvent extracts, very few compounds were detected in the aqueous extracts of the test coal sample obtained during leaching at high temperature and pressure (Table 3.14 and Table 3.15). The detected compounds included some hydrophilic compounds such as benzoic acid, dimethylphenols and phenol (Table 3.14). This is consistent with the data on TRH presented in Table 3.13, where only the TRH organic compounds with $<C_{15}$ were quantifiably released into aqueous extracts. The lack of detection of the organic compounds in the aqueous extracts could be either due to the inefficiency of water as an extractant or any matrix-related interference effects. This aspect was investigated further and is described below.

Table 3.14 Concentrations of organic compounds detected in aqueous leachates of the test coal (German Creek sample)

Compound	**LOR**	**Ultrapure water**	**SGW**	**[a]SGW + hydraulic fracturing fluid chemicals**			
				50°C	**100°C**	**Florisil®**	**SPE**
		Leachate concentration (mg/L)					
Benzoic acid	0.25	<LOR	<LOR	3.7±0.4	3.3	17±1	1.6±0.4
Dimethylphenol	0.1	<LOR	<LOR	56±12	87	135±8	87±26
Methylphenol	0.1	<LOR	<LOR	<LOR	<LOR	<LOR	0.3±0.04
Phenol	0.1	<LOR	<LOR	8.1±4.5	17	22±12	0.4±0.04

[a]*All leachates were produced at 10.3 MPa*

Considering that only a small number of test compounds were detected in aqueous extracts, a further test was carried out to assess how leachable these compounds were from the coal sample. The German Creek test coal sample and a clean sand (control sample) were spiked with known amounts of a selected set of compounds and were extracted using several aqueous extracts, ranging from ultrapure water to SGW, with and without the addition of hydraulic fracturing fluid chemicals.

The leaching efficiencies of aqueous extracts for different groups of compounds from the spiked coal in comparison with that from the sand matrix are presented in Table 3.15. In general, very poor recoveries of all compounds were noted in SGW extracts of coal. For most compounds these were less than 10% of what could be recovered from the inert sand (Appendix C, Figure C.2, Table 3.15). Only some relatively hydrophilic compounds such as phenolic compounds, naphthalene and benzoic acid showed somewhat higher recoveries, but only in the presence of hydraulic fracturing fluid chemicals. Similarly, the concentrations of low molecular weight organic compounds (C_{10}-C_{14} TRH) were higher in aqueous extracts containing hydraulic fracturing fluid chemicals (Table 3.14).

Table 3.15 Concentrations in mg/L and % recoveries (parentheses) of organic analytes in spiked coal, relative to spiked sand (matrix effect) in aqueous extracts with and without hydraulic fracturing fluid (10.3 MPa)

Compound	**Milli-Q water**	**Synthetic groundwater**	**Hydraulic fracturing fluid**				
			100°C	**50°C**	**Florisil®**	**SPE**	**Florisil®+SPE**
Acenaphthylene	nd (-)	nd (-)	nd (6±8)	nd (1±0.1)	nd (-)	nd (5±5)	nd (-)
Acenaphthene	nd (-)	nd (-)	nd (7±9)	nd (1±0.05)	nd (-)	nd (4±5)	nd (-)
Anthracene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (6±2)	nd (3±1)
Benzo[a]anthracene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (4±1)
Benzo[a]pyrene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Benzo[b,k]fluoranthene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Benzo[g,h,i]perylene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Benzoic acid	2.07±0.34 (11±17)	3.68±0.24 (5±1)	4.15±0.81 (79±20)	8.85±1.03 (42±12)	81.7±5.3 (21±14)	20.5±4.8 (8±1)	17.2±10.8 (8±1)
Chrysene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Dibenzo[a,h]anthracene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)

Compound	Milli-Q water	Synthetic groundwater	Hydraulic fracturing fluid				
			100°C	50°C	Florisil®	SPE	Florisil®+SPE
Dimethylphenol	2.16±0.59 (31±20)	4.31±1.39 (5±1)	1571±313 (6±1)	139±30 (40±21)	3816±230 (4±5)	515±151 (17±8)	1415±1420 (2±0.4)
Fluoranthene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Dibenzo[a,h]anthracene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Dimethylphenol	2.16±0.59 (31±20)	4.31±1.39 (5±1)	1571±313 (6±1)	139±30 (40±21)	3816±230 (4±5)	515±151 (17±8)	1415±1420 (2±0.4)
Fluoranthene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
Fluorene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)
o,p-Methylphenol	nd (8±12)	nd (7±1)	nd (-)	nd (69±40)	nd (38±9)	2.77±0.4 (11±2)	nd (12±2)
Naphthalene	nd (-)	nd (-)	nd (26±24)	nd (28±5)	nd (10±7)	nd (18±16)	nd (20±8)
Phenol	nd (-)	nd (-)	17.2±9.9 (-)	31±17 (-)	4.06±2.12 (-)	2.02±0.21 (18±5)	0.25 (91±40)
Pyrene	nd (-)	nd (-)	nd (-)	nd (-)	nd (-)	nd (3±2)	nd (3±1)

nd = no data

3.6 Leach test results – organic contaminants

3.6.1 General observations

Following leach test method optimisation, eight different coals (described earlier in Table 2.3) were extracted with synthetic groundwater solution (with and without hydraulic fracturing fluid) to assess the concentrations of organic compounds released and the variability among coal samples. The inclusion of hydraulic fracturing fluid markedly increased the concentration of organic substances leached into solution. For example, the TRH fraction C_{10}-C_{14} was detectable in all but one coal sample (i.e. Wandoan 2009) in the hydraulic fracturing solution leachates, whereas no TRH fractions were detectable in any of the SGW leachates (Table 3.16). Also, the full scan GC-MS analysis of the hydraulic fracturing solution leachates detected a greater diversity of compounds with considerably greater responses compared with the SGW leachates (Appendix C, Table C.3 and Table C.4, Figure C.3). The leachate data are discussed in more detail in the ensuing sections.

3.6.2 Concentrations of phenols and other target compounds

The study described in this report was conducted on coal samples that were stored for a limited period of time under conditions that were not optimal for the preservation of volatile organic compounds (e.g. BTEX). Studies focusing on volatile organic compounds require stringent controls on sample collection and analysis in order to limit losses of target compounds through volatilisation. Therefore no attempt was made to analyse BTEX and other volatile compounds in this study. The need for further work in this area is noted in Section 6 Knowledge gaps.

Of the remaining organic compounds selected for GC-MS/MS analysis (Appendix C, Table C.1) only phenolic compounds were detected, albeit at low concentrations, in the eight coal leachates. Data on phenol for the eight coals in aqueous extracts (SGW in the presence of hydraulic fracturing fluid) under standard conditions of pressure and temperature (10.3 MPa and 100°C) are presented in Figure 3.2 and Table 3.17 (see also Appendix C, Table C.5 and Table C.6). In all of the SGW coal leachates (in the absence of hydraulic fracturing fluid), the concentrations of phenol and other phenolic compounds were below the LOR (Table 3.17). However, when coals were leached with SGW + hydraulic fracturing fluid, the mean concentration of phenol in the eight coal leachates ranged from 135 to 346 µg/L. Nevertheless, due to high variability among the replicates, the differences in the mean values among the coals were not statistically significant.

Some other phenolic compounds, namely 2-methylphenol (o-cresol), 3-methylphenol (m-cresol) and 4-methylphenol (p-cresol), were also detected in the SGW+HFF leachates (Table 3.17). The median concentration of m-cresol plus p-cresol in the eight coal leachates was found to be 75±26 µg/L, whereas that of o-cresol was 21±7 µg/L.

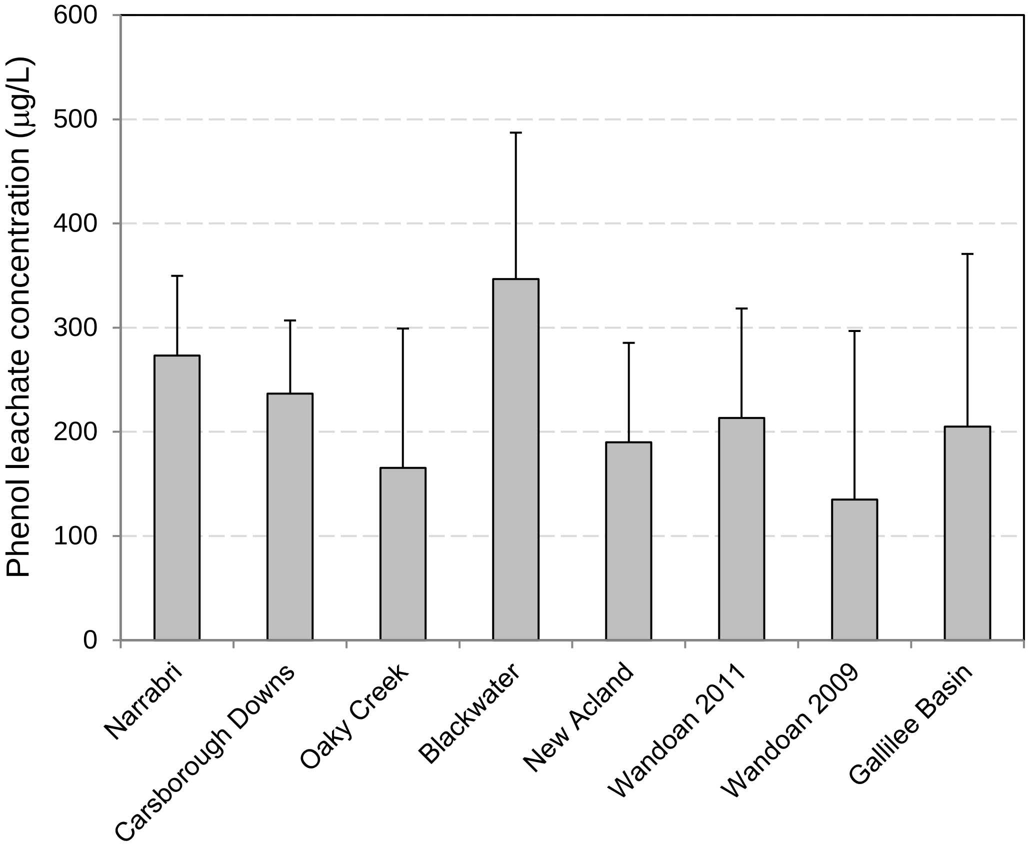


Figure 3.2 Concentrations of phenol from high pressure and temperature leaching of eight coal samples with synthetic groundwater + hydraulic fracturing fluids

Table 3.16 Summary of total recoverable hydrocarbon (TRH) fraction values for synthetic groundwater (SGW) and synthetic groundwater + hydraulic fracturing fluid (SGW + HFF) leachates collected from eight coal samples

Coal	**Leaching solution**	**TRH fraction (mg/L)**		
		C_{10}-C_{14}[a]	**C_{15}-C_{28}[b]**	**C_{29}-C_{36}[c]**
LOR[d]	***-***	***50***	***50***	***50***
Sand blank	SGW	<LOR	<LOR	<LOR
	SGW + HFF	52	<LOR	<LOR
Wandoan (2009)	SGW	<LOR	<LOR	<LOR
	SGW + HFF	<LOR	<LOR	<LOR
Wandoan (2011)	SGW	<LOR	<LOR	<LOR
	SGW + HFF	83	<LOR	<LOR
Blackwater	SGW	<LOR	<LOR	<LOR
	SGW + HFF	71	<LOR	<LOR
Oaky Creek	SGW	<LOR	<LOR	<LOR
	SGW + HFF	66	<LOR	<LOR
Carsborough Downs	SGW	<LOR	<LOR	<LOR
	SGW + HFF	73	<LOR	<LOR
Galilee Basin	SGW	<LOR	<LOR	<LOR
	SGW + HFF	58	<LOR	<LOR
Narrabri	SGW	<LOR	<LOR	<LOR
	SGW + HFF	59	<LOR	<LOR
New Acland	SGW	<LOR	<LOR	<LOR
	SGW + HFF	93	<LOR	<LOR

[a] fraction containing compounds with 10 to 14 carbon atoms. [b] fraction containing compounds with 15 to 28 carbon atoms. [c] fraction containing compounds with 29 to 36 carbon atoms. [d] LOR -limit of reporting (50 mg/kg)

The TRH data were generally consistent with the preliminary method optimisation experiments, where leachable concentrations of TRHs were only detectable in the C_{10}-C_{14} range and only in the SGW + HFF leachates (Table 3.17). For the SGW + HFF treatment, New Acland coal had the highest TRH C_{10}-C_{14} concentration of 93 mg/kg (Table 3.17). The chemicals used in the hydraulic fracturing fluid, such as Ethylene glycol monobutyl or butoxyethanol, also contributed to the TRH pool, as indicated by their detection in the leachate from the sand blank. In contrast, no TRHs were detectable in any of the SGW leachates.

Table 3.17 A summary of organic compounds detected in leachates from eight different coals in ‘synthetic groundwater’ (SGW) and SGW + fracturing fluid chemicals (HFF)

Coal source	**Leachate type**	**Phenol (µg/L)**	**o-cresol (µg/L)**	**m-cresol plus p-cresol (µg/L)**	**TRH C_{10}-C_{14} (mg/L)**	**Number of compounds**
LOR	**-**	***10***	***10***	***20***	***50***	**-**
Wandoan (2009)	SGW	<LOR	<LOR	<LOR	<LOR	4
	SGW + HFF	135	23	68	<50	8
Wandoan (2011)	SGW	<LOR	<LOR	<LOR	<LOR	4
	SGW + HFF	213	19	76	83	12
Blackwater	SGW	<LOR	<LOR	<LOR	<50	8
	SGW + HFF	347	28	95	71	8
Oaky Creek	SGW	<LOR	<LOR	<LOR	<LOR	3
	SGW + HFF	165	25	104	66	13
Carsborough Downs	SGW	<LOR	<LOR	<LOR	<LOR	7
	SGW + HFF	237	22	78	73	14
Galilee Basin	SGW	<LOR	<LOR	<LOR	<LOR	4
	SGW + HFF	205	22	73	58	9
Narrabri	SGW	<LOR	<LOR	<LOR	<LOR	4
	SGW + HFF	273	23	83	59	12
New Acland	SGW	<LOR	<LOR	<LOR	<LOR	2
	SGW + HFF	190	20	63	93	8

3.6.3 Non-target compounds identified using GC-MS library screen

The GC-MS library screen indicated that a greater number of organic compounds occurred where SGW was mixed with HFF (SGW + HFF), compared with SGW alone (Appendix C, Table C.3 and Table C.4). The intensity of the peaks, was also greater in the SGW + HFF leachates (Appendix C, Figure C.3). A higher concentration of TRH load in the SGW + HFF leachates was also greater than that of the SGW on its own (Table 3.17). The diversity, in terms of physicochemical properties (such as structural composition and K_{ow}), was greater for the organic compounds identified in the SGW + HFF leachates.

In the case of the organic compounds detected in the SGW + HFF leachates, it is not clear if they originated from coal or hydraulic fracturing fluid components or due to interactions between the coal and hydraulic fracturing fluid components. For example, the compounds may have been due to the hydraulic fracturing fluid components transforming due to the heat and/or pressure conditions of leaching or due to the coal and hydraulic fracturing fluid components reacting together. For the majority of the organic compounds identified in both SGW and SGW + HFF leachates, little information about their ecotoxicity or potential impact on the environment is currently available in the literature.

Table 3.18 Major organic compounds detected in synthetic groundwater (SGW) and synthetic groundwater+ hydraulic fracturing fluid (SGW + HFF) leachate extracts from any of the eight coals. The compounds were identified using a NIST library search

Synthetic groundwater (SGW)	**CAS number**
1,1-dimethylcyclohexane	590-66-9
1-ethyl-2-methyl cyclohexane	4923-78-8
heptadecane	629-78-7
3-methyl buten-2-al	107-86-8
(1-methylhexylidene) methylamine	22058-71-5
1-methyl-7-(methylethyl)phenanthrene	483-65-8
methylnonadecane	NA
1-methyl-2-propyl cyclohexane	4291-79-6
nonadecane	629-92-5
octacosane	630-02-4
1,2,3,4,5-pentamethylcyclopentane	33189-46-7
propylcyclopentanone	NA
tetradecane	629-59-4
tetramethyl-5-dicynediol	NA
4,4,6-trimethylcyclohexen-1-ol	21592-95-0
Synthetic groundwater + hydraulic fracturing fluid (SGW + HFF)	**CAS number**
3,3,5-trimethyl cyclohexenone	78-59-1
dodecyl acrylate	2156-97-0
hexadecyl acrlyate	13402-02-3
limonene glycol	1946-00-5
4-methyl 2,3-dihydrofuran	34314-83-5
methylbenzene	108-88-3
2-methyl-2-(3-methyl-1-vinyl-2-butenyl)oxirane	NA
octadecane	593-45-3
terpinene	99-86-5
tetracontane	7098-22-8
verbenol	473-67-6

4 Discussion

4.1 Release of inorganic contaminants

The aims of this part of the study were to identify factors affecting contaminant release from coal seams during hydraulic fracturing operations. Laboratory-based investigations were conducted in order to control a number of important variables and characterise their effects on contaminant release. Overall, the study can be viewed as providing upper bound concentration data for a range of inorganic contaminants that can inform future monitoring based studies and further laboratory investigations.

Detectable concentrations of trace elements were measured in leachates from a range of representative Australian coals under controlled laboratory conditions. It was noted that there was considerable variability between coal types both in terms of the total content of trace elements and the concentrations of elements leached into solution. Further studies are required to characterise the extent of this variability both on a regional (spatially within one coal formation) and national spatial scale. The underlying relationships between trace element content and the physico-chemical properties of coal (e.g. coal rank) also need to be investigated.

The following factors were noted to influence trace element release into solution: pH, temperature and the presence of complexing agents. The citrate complexing agent used in this study was shown to increase the release of several metals including iron and aluminium. Unfortunately, the pressure extraction apparatus used for the organic contaminants work was not compatible with the analysis of trace elements as it had a stainless steel extraction cell. Consequently, the study did not cover the effects of pressure on trace element mobilisation.

Radionuclide concentrations (i.e. radium, thorium and uranium) were generally low and below concentrations of regulatory concern based on their radioactive properties. However, as noted in a literature review of geogenic contaminants (Apte et al. 2017), the pre-concentration of radionuclides in scale formations in pipework and other deposits is a known problem in the oil and gas industry as it affords a means by which radionuclides may be pre-concentrated above ground. The data from this study suggest that radionuclides would have to be pre-concentrated substantially before there would be concerns over radiological safety. Aside from pre-concentration in pipework and other infrastructure, the concentration of radionuclides in reverse osmosis waste products (such as brines), and in microfiltration and reverse osmosis filters and membranes, is worthy of further investigation.

Benchmarking of leachate data against Australia and New Zealand water quality guidelines for aquatic ecosystem protection (ANZECC and ARMCANZ 2000) provided the means by which the potential significance of the findings could be assessed. It should be noted that the laboratory studies were not intended to predict environmental concentrations in coal seam gas wastewaters. Important factors such as dilution, and environmental transformations that may reduce contaminants concentrations are not considered. Comparison of the laboratory data against the water quality guideline benchmarks indicated that the geogenic contaminants of most potential concern are as follows: aluminium, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, lead, manganese, nickel, selenium, silver, thallium, uranium, vanadium and zinc.

It should be noted that only 25 benchmark values were available from the guidelines. Thus the potential role of less common trace elements as contaminants of concern cannot be ruled out. For instance, barium concentrations were present in relatively high concentrations (e.g.

up to 1100 µg/L in the pH 5 leach test) but no Australia or New Zealand water quality guideline for aquatic ecosystem protection was available for comparative purposes.

There are limited field data sets available for comparison to the results of the leach tests. However, NICNAS have recently published a compilation of field data for flowback and produced waters at undisclosed coal seam gas sites in Queensland (NICNAS 2014). Water quality data was reported for a total of 64 wells with and without hydraulic fracturing. The data indicated that the following elements exceeded the ANZECC and ARMCANZ water quality guidelines for aquatic ecosystem protection in some of the water collected: aluminium, arsenic, boron, chromium, copper, selenium, vanadium and zinc. This has remarkable overlap with the elements identified in the leach tests and confirms the importance of geogenic contaminants that are released into flowback waters.

Although most of the leach tests applied were designed to be harsh and give an upper bound estimate of likely contaminants release, the results obtained with the SGW buffered pH 7 (40^{o}C, atmospheric pressure) are worthy of special consideration. Even under these relatively mild extraction conditions, dissolved copper, selenium, uranium and vanadium concentrations exceed their respective guideline values in one or more of the coal leachate samples. It appears that equilibration with warm groundwater is sufficient to mobilise these contaminants from some Australian coal seams.

Sulfate was also released from the coal samples in mg/L concentrations. While this is not an issue in terms of toxicity, the influence of elevated sulfate concentrations on microbiological processes may be worthy of future consideration. Particularly because under conditions of oxygen depletion, elevated sulfate concentrations are likely to favour anaerobic bacterial processes that lead to toxic hydrogen sulfide production.

It should be noted that some trace elements may exert impacts on aquatic ecosystems through food-chain bioaccumulation. In this instance, the use of water quality guidelines that are derived from toxicity test data as benchmark will not be adequate to ensure environmental protection. The two most important elements falling into this category are mercury (Morel et al. 1999) and selenium (Chapman et al. 2009). Mercury concentrations were extremely low in all leachates analysed, however, the concentration of selenium were much higher. Closer attention to the behavior of this element in any future studies would therefore be merited.

This study did not consider any attenuation processes occurring in natural systems that may reduce the concentration of geogenic contaminants. Dilution will play a major role as well as changes in pH, temperature and pressure. It is also likely that some contaminants will be lost from solution through the process of adsorption onto various mineral phases. Other sources of geogenic contaminants need also to be taken into account. These will include groundwater draining mineralised areas.

4.2 Release of organic contaminants

Phenol and cresols were the compounds that were detected in all coal samples during leaching with synthetic groundwater amended with hydraulic fracturing fluid. In the leachates with the synthetic groundwater alone, these compounds were not detected. In the presence of hydraulic fracturing chemicals, the median concentration of phenol in the eight coals was 220±120 µg/L. The median concentrations of cresols were much lower and ranged from 21±7 to 75±26 µg/L in the eight coal samples.

Phenolic compounds are important from water quality perspective for a number of reasons, including their higher solubility (and therefore higher release), leading to potential higher concentrations in the environment, and a commensurate increase in their toxicological impact on human and ecosystem health (Orem et al. 2007). For some of the compounds, water quality guidelines have been established that are crucial for regulation and risk management of these geogenic contaminants.

To address the question, as to what the detected concentrations of phenol and cresols may mean in terms of environmental impact, leachate concentrations were compared against the Australian guideline value for phenol (ANZECC and ARMCANZ 2000). Even without taking into account the dilution in the aquifers (and in the receiving environments), the above median concentration of phenol in the leachates from the eight coals is approximately 1.5 to 2 times below the guideline values for freshwater (320 µg/L) and marine ecosystems (400 µg/L) for 95% species protection (ANZECC and ARMCANZ 2000). The potential risks associated with phenols could be more accurately assessed with data from field studies.

For cresols, currently there are no guideline values available in Australia. However, the Canadian water quality guidelines for a group of phenolic compounds including monohydric (e.g. phenol, cresols and xylenols) and dihydric phenols (e.g. catechols and resorcinols) recommend a threshold of 4.0µg/L for protecting aquatic life in freshwater ecosystems (Canadian Council of Ministers of the Environment (CCME) 1999). The toxicity of phenols is assumed to be additive due to their similar mode of action (CCME 1999). Clearly, the sum of concentrations of monohydric phenolic compounds detected in these coal leachates exceeded the above guideline value by an order of magnitude. This does not consider any dilution in the receiving environment.

The synthetic groundwater did not favour the transfer of organic compounds from coal into the leachate, because the carbonaceous materials, such as coal, generally have a high affinity for organic compounds (Cornelissen et al. 2005). This is especially the case for hydrophobic organic compounds (high K_{ow}) such as PAHs, because such chemical compounds of similar character preferentially associate with one another (Koelmans et al. 2006; Schwarzenbach et al. 2003). The profile of organic compounds in aqueous leachates is therefore expected to be predominantly compounds with higher water solubility and polarity, and lower molecular weight (Schulz et al. 1997). This is demonstrated by the recovery experiments where, although recoveries were comparatively low, the organic compounds with higher water solubility (hydrophilic) and lower log K_{ow} were detectable in the leachates (Table 3.15 and Table 3.16). The presence of hydraulic fracturing chemicals facilitated the release of hydrophilic compounds (such as phenolic compounds) in this study. However, the hydraulic fracturing mixture composition used in this study was estimated from the limited information available on actual hydraulic fracturing fluid composition.

A factor that influenced the recovery efficiencies of the organic compounds in aqueous leachates was the temperature of the leaching solution (Table 3.15). The solubility of organic compounds has been found to be dependent on the pressure and temperature of the solution, although this is highly dependent on the nature of the compound itself (Arias-Gonzalez et al. 2010; Reza & Trejo 2004; Sawamura 2007). The efficiency of benzoic acid recovery was higher at 100°C, while recovery efficiency decreased for dimethylphenols at the higher temperature (Table 3.15). In the case of naphthalene, however, there was no effect from variation in temperature. While this study only considered one elevated leaching pressure (10.3 MPa) and two leaching temperatures (50°C and 100°C) only during optimisation steps, this result would suggest that temperature may have an effect on the leaching efficiency of the aqueous solutions. It would therefore be important to systematically assess the effect on the leaching efficiencies of organic compounds of temperatures and pressures, reflecting the conditions associated with hydraulic fracturing operations in Australia. Monitoring data from coal seam gas extraction operations could, potentially, inform these investigations.

The aqueous leachates obtained with SGW mixed with hydraulic fracturing fluid contained many more organic compounds than those in the SGW alone, based on the GC-MS library screen. However, aside from the structurally related 4,4,6-trimethylcyclohexen-1-ol and

3,3,5-trimethyl cyclohexenone detected in the SGW and hydraulic fracturing fluid leachates, respectively, there was no overlap in the detected chemicals in the two different leachates (Table 3.18). The table only summarises compounds that were not also detected in sand blanks (see Appendix C, Table C.3). The detection of compounds in SGW that were not detected in SGW + HFF is likely to have been due to their signal being obscured by the dominant and complex signal of compounds present in hydraulic fracturing fluid (see Appendix C, Table C.4 and Figure C.3). The peak intensity in the hydraulic fracturing fluid chromatograms was also substantially greater (Appendix C, Figure C.3). It is therefore likely that even if the same compounds were present in both types of leachate, the signal of the compounds present in the hydraulic fracturing fluid leachate chromatograms would have interfered with the detection of geogenic substances.

Surprisingly, a number of highly hydrophobic and water-insoluble compounds, such as octadecane and tetracontane, were also found in a limited number of hydraulic fracturing fluid leachates (Appendix C, Table C.4). With the exception of 3-methylbuten-2-al, the compounds detected in the SGW leachates were either slightly soluble to insoluble in water (SRC 2014), with correspondingly moderate to high octanol-water coefficients (log K_{ow}). This suggests that the transport of these compounds via dissolution in the SGW leachate would be unlikely and other transport mechanisms, such as association with dispersed and colloidal solids, may be occurring (Volk et al. 2011). In contrast to the hydraulic fracturing fluid, SGW had no organic compounds present in the leaching solution, suggesting that the organic compounds detected in the SGW leachates were likely to be geogenic in nature, albeit at low concentrations.

Although the potential formation of new compounds due to the interactions of hydraulic fracturing fluid and coals was not the main objective of this study, some observations are noteworthy. Half of the 14 compounds detected in at least three of the eight coals in the hydraulic fracturing fluid leachates belonged to the monoterpene class of chemicals and 10 of the detected compounds were detected in both the control (sand blank) and coal leachates (Appendix C, Table C.4). Monoterpenes and butoxyethanol were absent in the SGW leachates (Appendix C, Table C.3). The hydraulic fracturing fluid was therefore likely to have made a substantial contribution to the number of compounds detected in the leachates. Furthermore, there was evidence that a number of the chemicals in the hydraulic fracturing fluid were likely to have been chemically transformed during the leaching process. For example, the monoterpenes carvone, linalool and mentha-1,8-dienol are all structurally related to limonene and were present in both the sand blanks and majority of coal leachates. Limonene glycol is similarly structurally related to limonene, although it was not detected in the sand blanks suggesting that some interaction with the coal was required for its formation. This may have also been the case with dodecyl acrylate and hexadecyl acrylate being formed in the presence of polyacrylate from the hydraulic fracturing solution and coal. While the formation of new compounds due to complex interactions of coal with hydraulic fracturing fluid chemicals under temperature and pressure conditions used in this study was observed, a much more systematic study using high resolution mass spectrometry is needed to confirm this important phenomenon.

Significant concentrations of TRH in the C_{10}-C_{14} fraction in SGW + HFF leachates were noted in the coal samples (Table 3.17), and monoterpenes described above contributed to this pool. Other substances with lower carbon chain (not contributing to the above), such as 3,3,5-trimethyl cyclohexenone, 4-methyl-2,3-dihydrofuran and methylbenzene were also detected. However, it was not possible to determine whether the compounds leached within the C_{10}-C_{14} fraction were geogenic, derived from the hydraulic fracturing fluid or were formed following the interaction between the geogenic compounds in coal and hydraulic fracturing fluid A more detailed assessment of the variables under which the coal and hydraulic fracturing compounds interact, would be desirable.

An organic compound of note, with <10 carbon atoms, was methylbenzene (toluene), which is a component of BTEX group of aromatic hydrocarbons. Toluene was detected in the Oaky Creek coal hydraulic fracturing fluid leachate (Table C.4). Formation water produced from North American and European hydraulic fracturing operations have also detected trace levels of toluene in produced water (Gross et al. 2013; Harrison et al. 2006; Meiners et al. 2012), although there is no available evidence of this occurring in Australian coal seam gas operations (Volk et al. 2011). The presence of toluene in the leachate, as with any of the compounds identified by the qualitative screening, would need to be confirmed through further targeted investigations to confirm their presence quantitatively. The coal samples used in this study were sourced from a CSIRO bulk sample store and therefore were not suitable for the analysis of volatile organic compounds.

The concentrations of organic contaminants in flowback or produced water are likely to be time-dependent. Therefore, the limited overseas data on organic contaminants in produced water (e.g. Orem et al. 2007) and those reported here are only indicative of what might be present in flowback or produced waters. The identification of phenols and several other compounds in our study are consistent with the data reported by Orem et al. (2007). However, the limited data that were available on flowback and/or produced water in the survey conducted by NICNAS (2014), phenol concentrations were found to be below LOD (10 µg/L) in water samples from both hydraulically fractured and non-hydraulically fractured wells. Only TRH (C_{10}-C_{36}) were detected in water samples from both the hydraulically fractured wells and the non-hydraulically fractured wells.

5 Conclusions

Detectable concentrations of over 60 trace elements were observed in the laboratory-based leach tests conducted on a range of Australian coal samples. These data may be viewed as upper bound estimates of geogenic contaminant release from coal seams undergoing gas extraction.

The elevated temperature and pressure in groundwater during the hydraulic fracturing process appears to play a role in the mobilisation of organic substances. However, the effects were found to be compound specific. A systematic investigation is needed under conditions relevant to hydraulic fracturing in Australia.

Large variability was observed between coal types, in the measured trace element and organics concentrations in both the whole coals and in their leachates. This emphasises the need for site-specific investigations to ascertain the risk posed by geogenic contaminants at a given coal seam gas operation.

Based on their measured concentrations in the laboratory-based leaching studies and comparison with surface water quality benchmarks for aquatic ecosystem protection, the following inorganic geogenic contaminants have been identified as priorities for further investigations: aluminium, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, lead, manganese, nickel, selenium, silver, thallium, uranium, vanadium and zinc

It should be noted that water quality benchmarks for drinking water, aquatic environments, and stock watering are not available for a number of trace elements that were found in the leachates (i.e. barium).

Radionuclide concentrations (i.e. radium, thorium, and uranium) in the leachates generated from the coal samples tested were very low and, based on their radioactive properties, were below concentrations of regulatory concern. However, this does not preclude the pre-concentration of radionuclides in precipitates forming in flowback and produced water ponds, gathering lines and pipeworks, or during water treatment (e.g. in micro-filtration filters and reverse osmosis membranes).

Phenol and cresols (methylphenols) were the most commonly detected compounds in coal samples leached with synthetic groundwater, particularly in the presence of the hydraulic fracturing fluid chemicals. The median concentration of phenol in leachates (before dilution with groundwater) was 220±120 µg/L, below the water quality guideline value of 320 µg/L for 95% species protection (ANZECC and ARMCANZ 2000). The median concentrations of o-cresols and m- plus p-cresols were 21 and 75 µg/L, respectively. However, these concentrations exceed the Canadian water quality guidelines for monohydric phenols (which include phenol and cresols among other compounds)

Higher concentrations of phenols and other low molecular weight total recoverable hydrocarbons (TRHs) in the C_{10}-C_{14} range were released on leaching of coal samples with synthetic groundwater mixed with hydraulic fracturing fluid at high temperature and pressure compared to leaching with synthetic groundwater.

Based on GC-MS library searches a further 14 organic compounds were identified in the coal leachates, but their origin (geogenic or not) is not clear. Generally, a greater number of compounds (as indicated by the C_{10}-C_{14} TRH load) were detected in the presence of hydraulic fracturing fluid. Formation of new compounds due to the interaction of coal and hydraulic fracturing fluid was noted and needs further investigation. Furthermore, the ecological relevance, in terms of their environmental fate and ecological effects, of the identified organic compounds is not well understood and needs to be addressed.

The complex mixtures of organic chemicals released from coals present significant analytical challenges including achieving adequate sensitivity and elimination of matrix interference. Further work is needed to develop more sensitive, specific and robust analytical methods.

6 References

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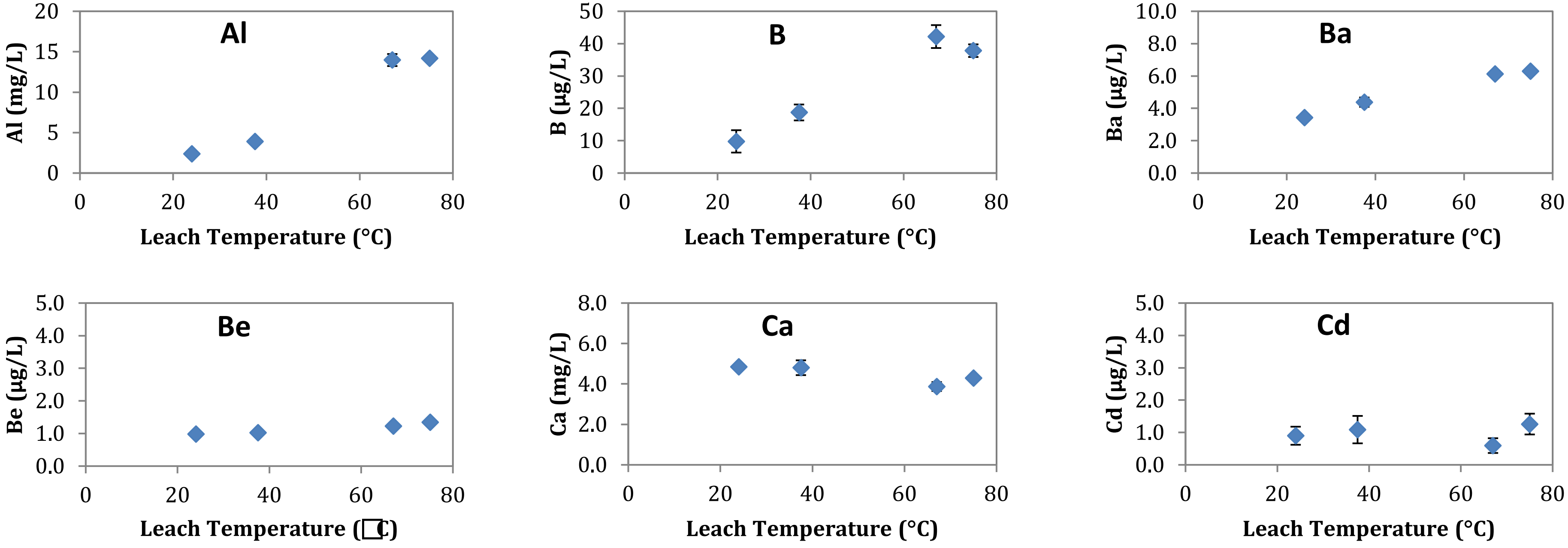
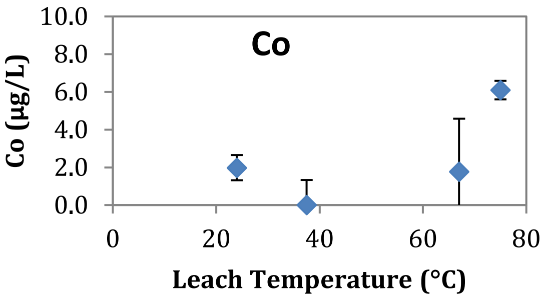
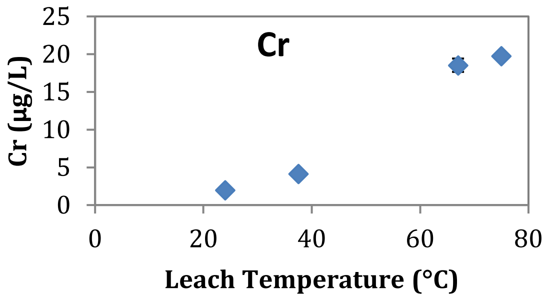
Appendix A - Leach test optimisation studies

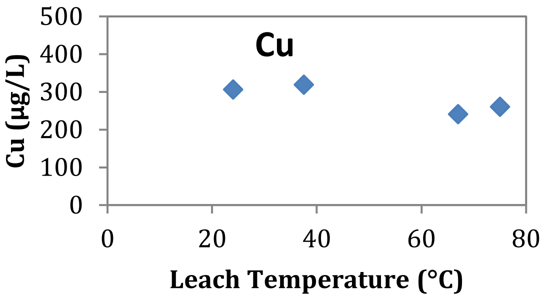
Optimisation of leach test – temperature

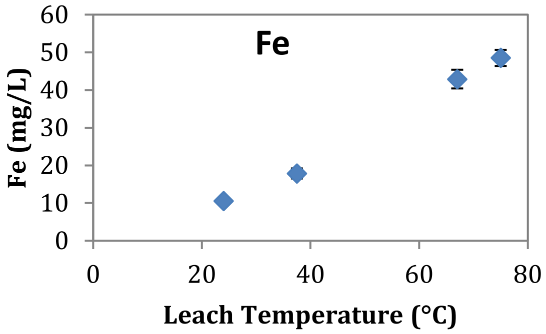
Leach test optimisation: graphs showing the effect of temperature on trace element release from coal (error bars are ± one standard deviation).

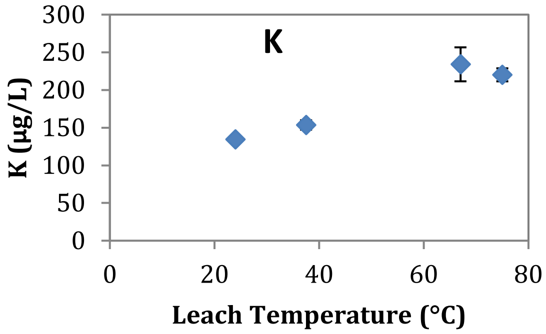


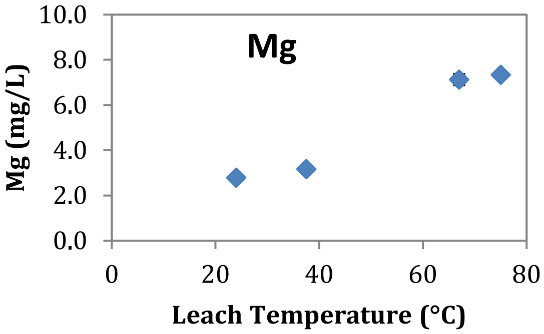

Co
Co (µg/L)
10.0
8.0
6.0
4.0
2.0
0.0
0
20
40
60
80
Leach Temperature (°C)

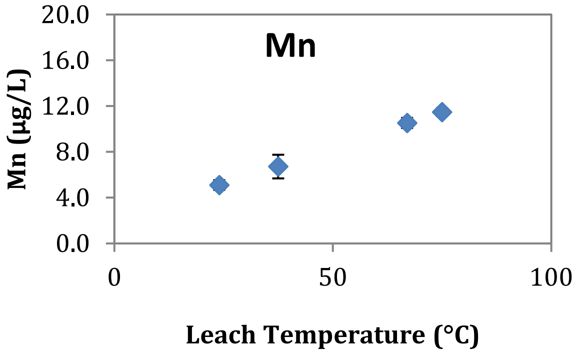

Cr
Cr (µg/L)
25
20
15
10
5
0
0
20
40
60
80
Leach Temperature (°C)

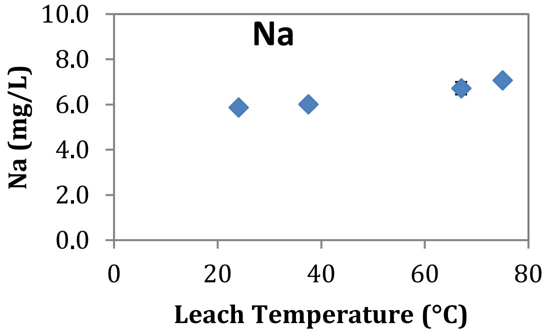

Cu
Cu (µg/L)
500
400
300
200
100
0
0
20
40
60
80
Leach Temperature (°C)

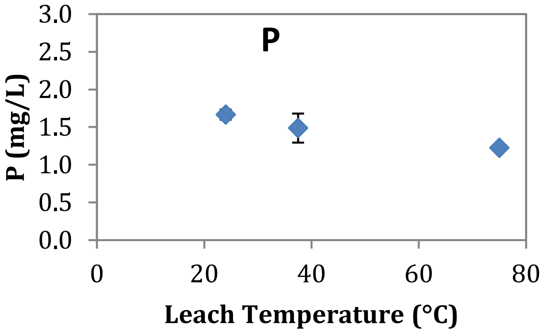

Fe
Fe (mg/L)
60
50
40
30
20
10
0
0
20
40
60
80
Leach Temperature (°C)

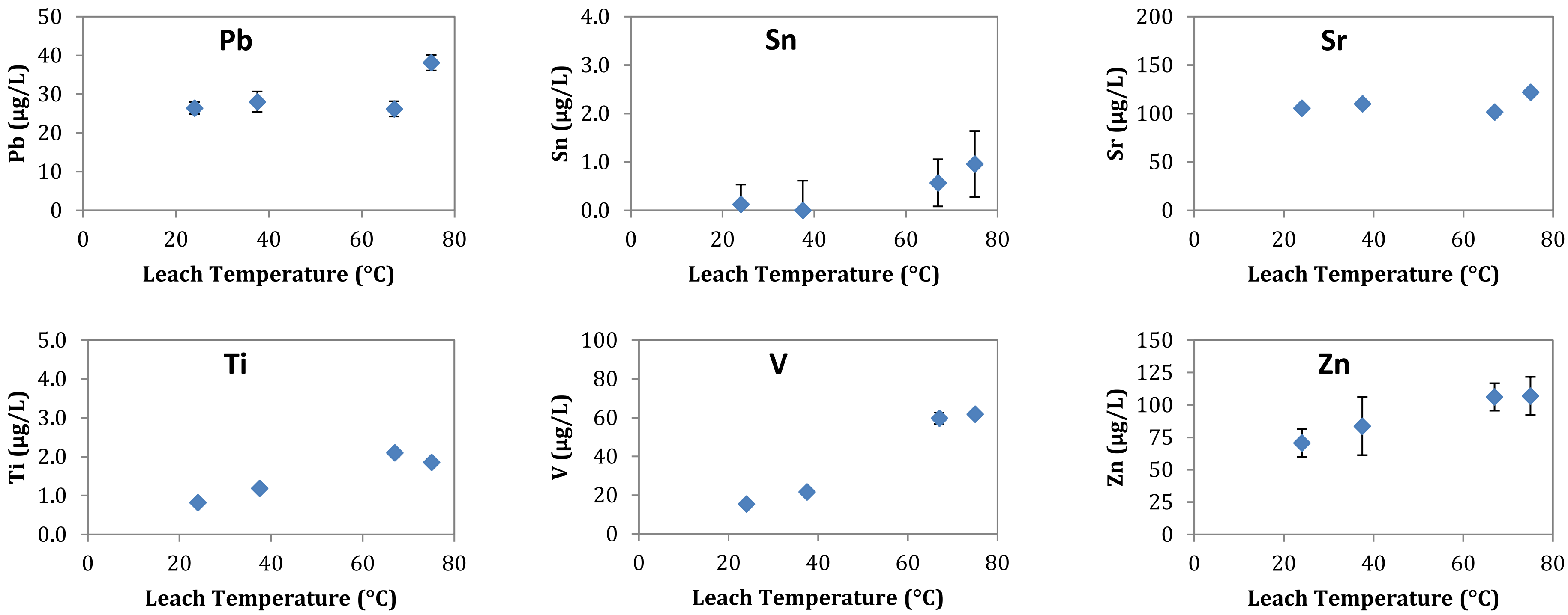

K
K (µg/L)
300
250
200
150
100
50
0
0
20
40
60
80
Leach Temperature (°C)


Mg
Mg (mg/L)
10.0
8.0
6.0
4.0
2.0
0.0
0
20
40
60
80
Leach Temperature (°C)


Mn
Mn (µg/L)
20.0
16.0
12.0
8.0
4.0
0.0
0
50
100
Leach Temperature (°C)

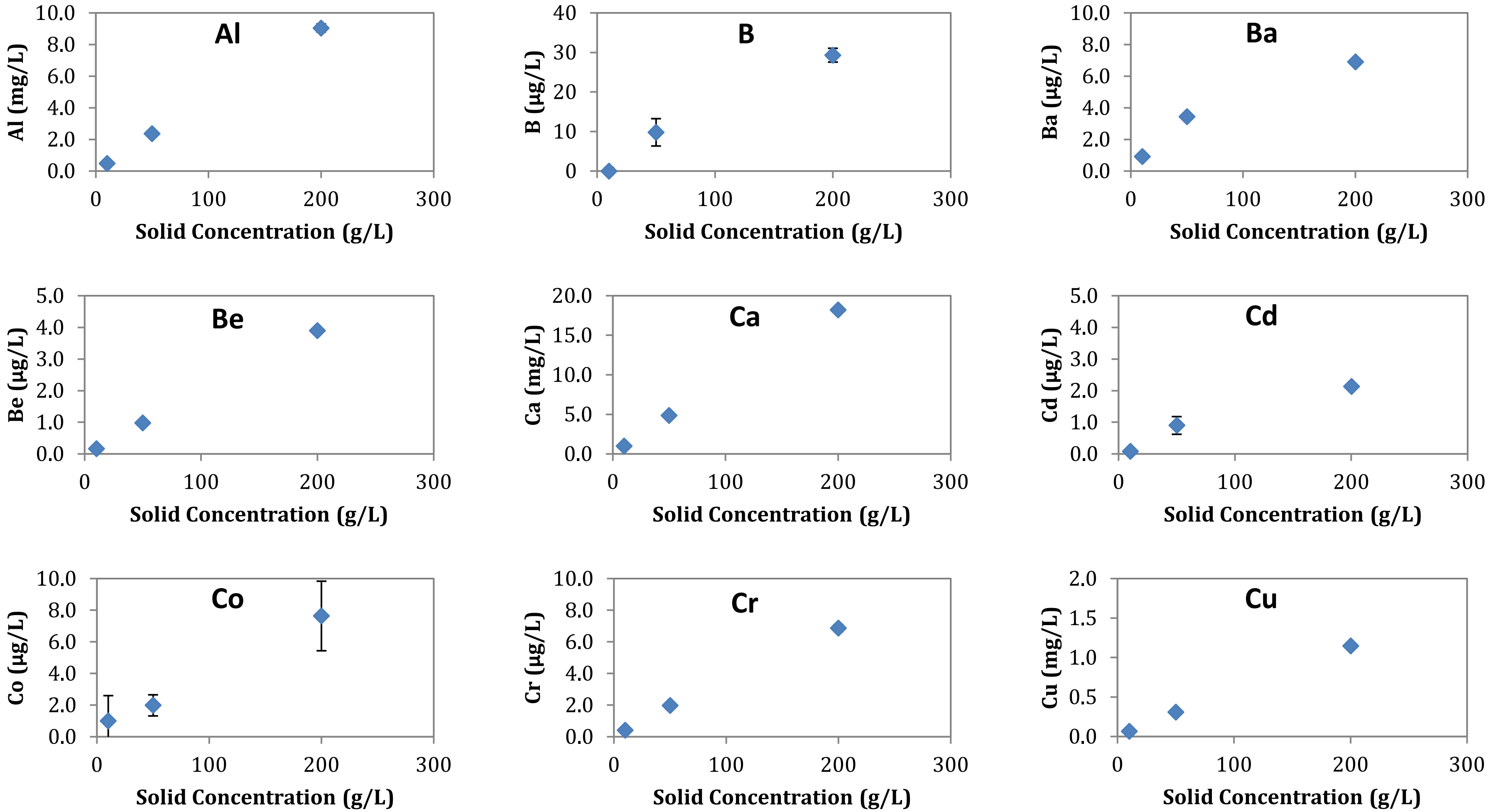

Na
Na (mg/L)
10.0
8.0
6.0
4.0
2.0
0.0
0
20
40
60
80
Leach Temperature (°C)

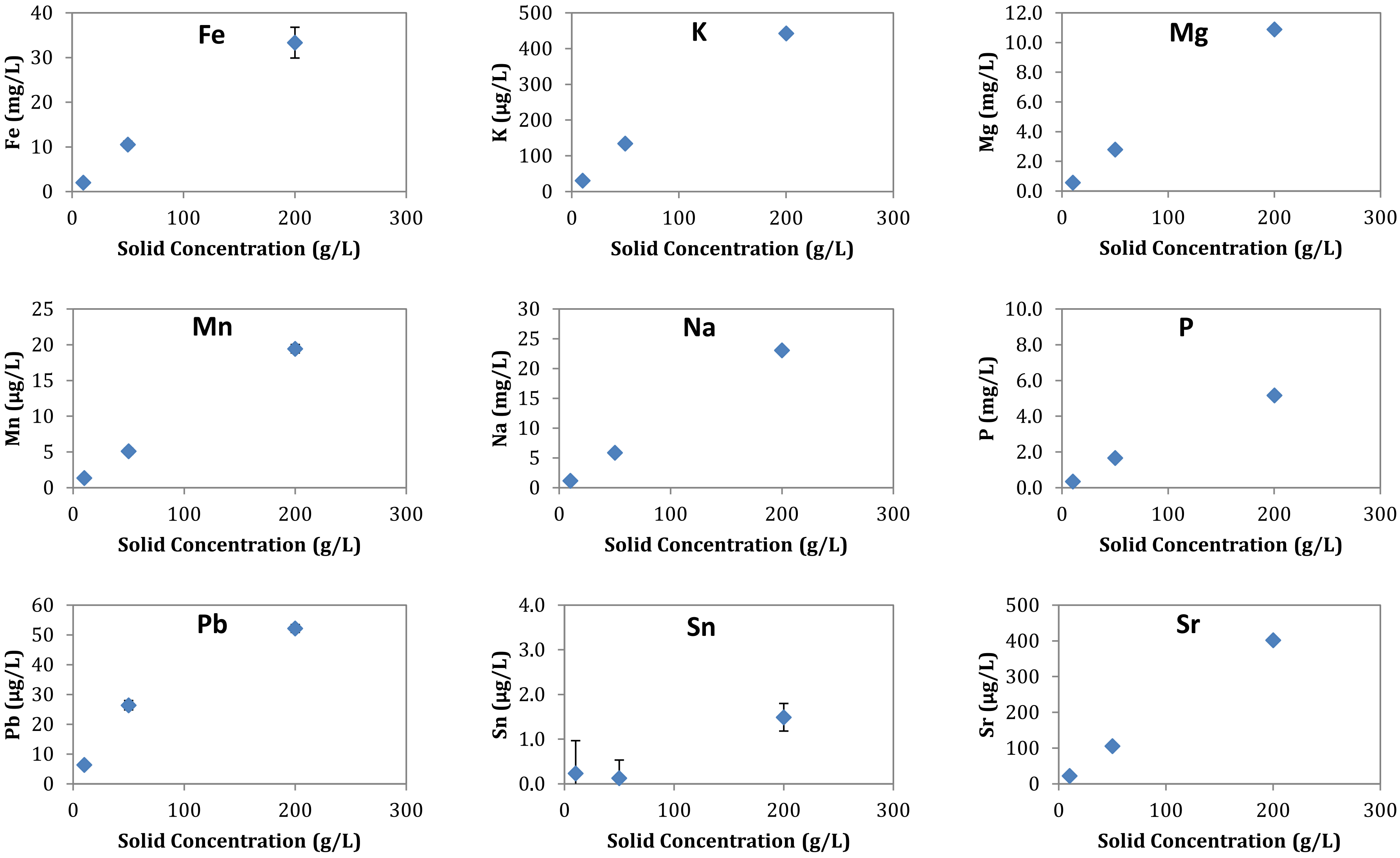

P
P (mg/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
Leach Temperature (°C)

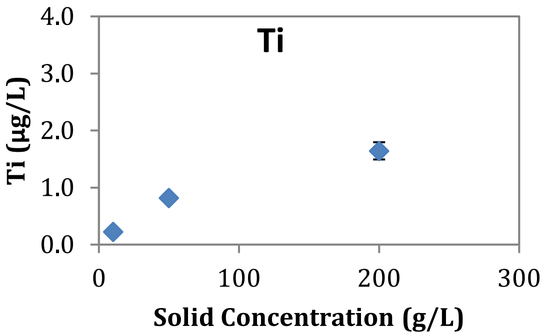

Pb
Pb (µg/L)
50
40
30
20
10
0
0
20
40
60
80
Leach Temperature (°C)
Sn
Sn (µg/L)
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
Leach Temperature (°C)
Sr
Sr (µg/L)
200
150
100
50
0
0
20
40
60
80
Leach Temperature (°C)
Ti
Ti (µg/L)
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
Leach Temperature (°C)
V
V (µg/L)
100
80
60
40
20
0
0
20
40
60
80
Leach Temperature (°C)
Zn
Zn (µg/L)
150
125
100
75
50
25
0
0
20
40
60
80
Leach Temperature (°C)

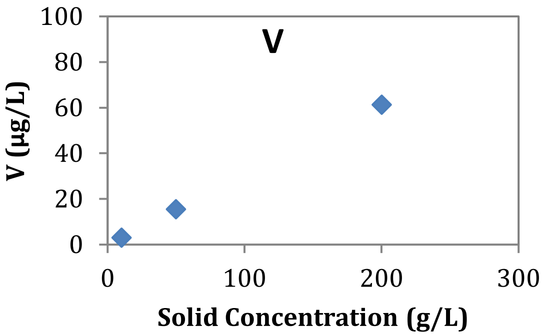
Optimisation of leach test – solids concentration

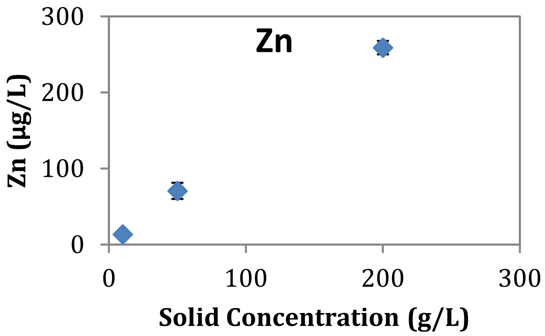
Leach test optimisation: effect of solids concentration on trace element release from coal (error bars are ± one standard deviation.




Fe
Fe (mg/L)
0
10
20
30
40
K
K (µg/L)
0
100
200
300
400
500
Mg
Mg (mg/L)
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Mn
Mn (µg/L)
0
5
10
15
20
25
Na
Na (mg/L)
0
5
10
15
20
25
30
P
P (mg/L)
0.0
2.0
4.0
6.0
8.0
10.0
Pb
Pb (µg/L)
0
10
20
30
40
50
60
Sn
Sn (µg/L)
0.0
1.0
2.0
3.0
4.0
Sr
Sr (µg/L)
0
100
200
300
400
500
0
100
200
300
Solid Concentration (g/L)

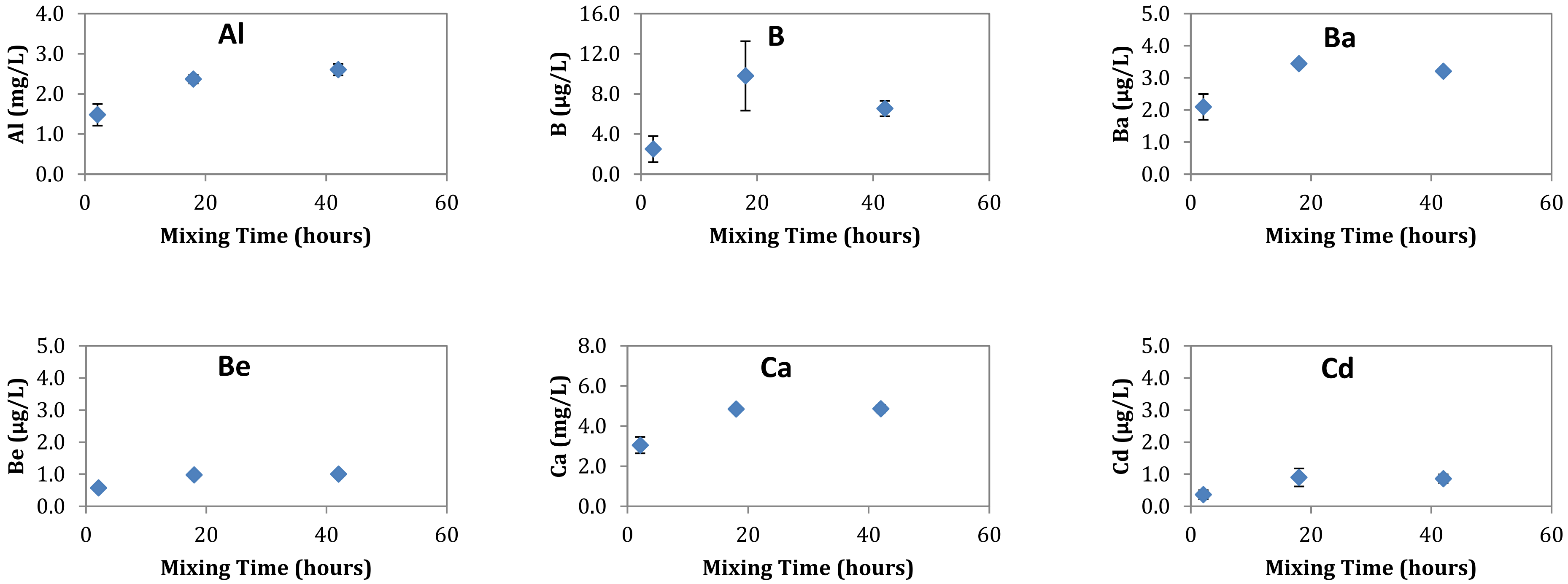

Ti
Ti (µg/L)
4.0
3.0
2.0
1.0
0.0
0
100
200
300
Solid Concentration (g/L)

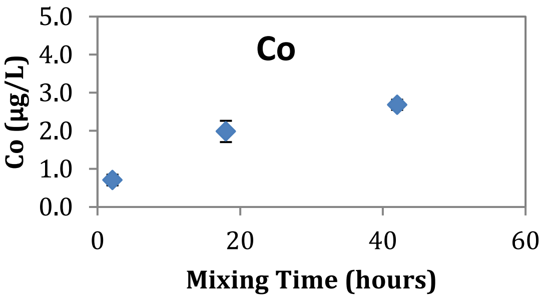

V
V (µg/L)
100
80
60
40
20
0
0
100
200
300
Solid Concentration (g/L)

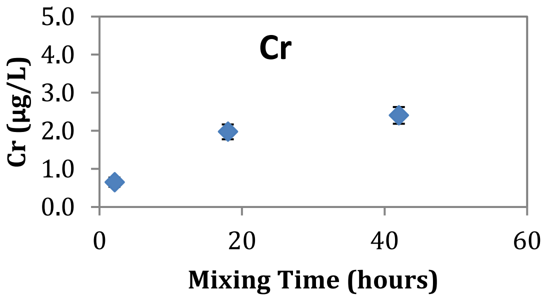

Zn
Zn (µg/L)
300
200
100
0
0
100
200
300
Solid Concentration (g/L)

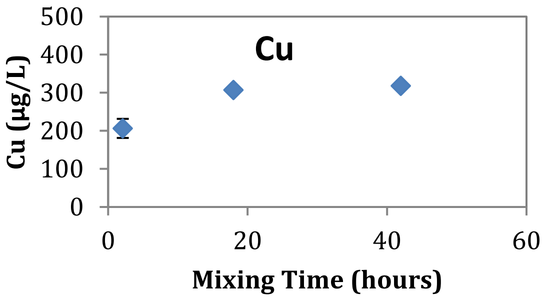
Optimisation of leach test – mixing time

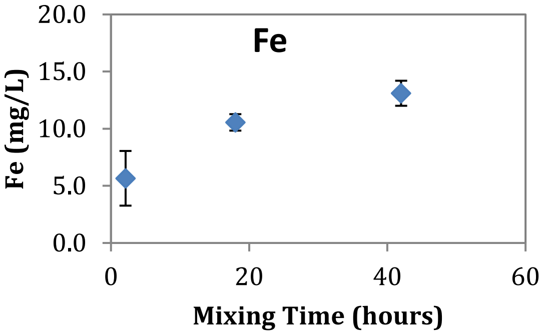
Leach test optimisation: effect of mixing time on trace element release from coal (error bars are ± one standard deviation).

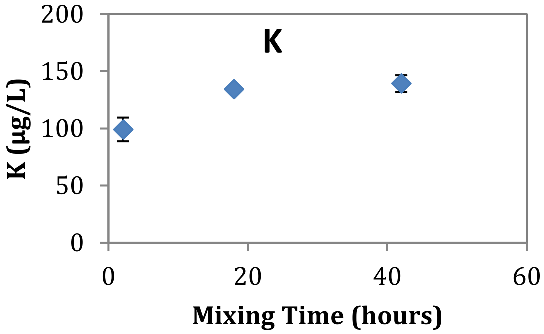


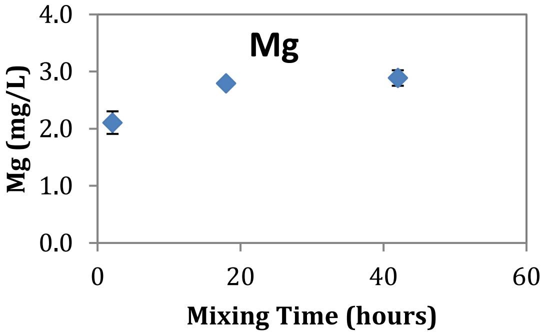

Co
Co (µg/L)
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
Mixing Time (hours)

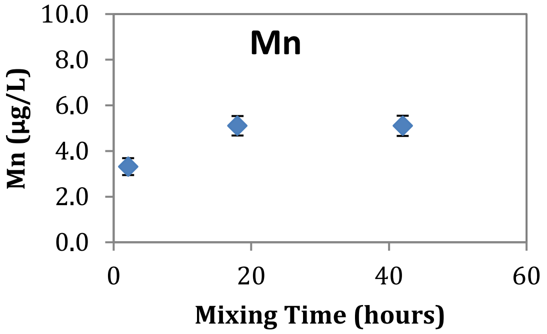

Cr
Cr (µg/L)
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
Mixing Time (hours)

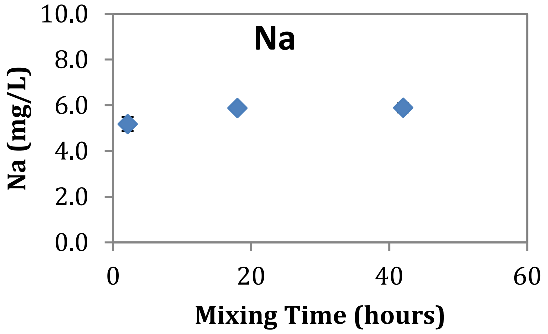

Cu
Cu (µg/L)
500
400
300
200
100
0
0
20
40
60
Mixing Time (hours)

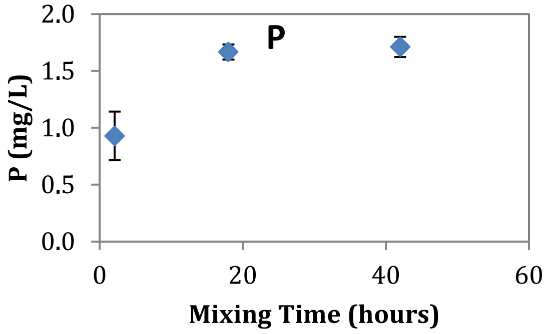

Fe
Fe (mg/L)
20.0
15.0
10.0
5.0
0.0
0
20
40
60
Mixing Time (hours)

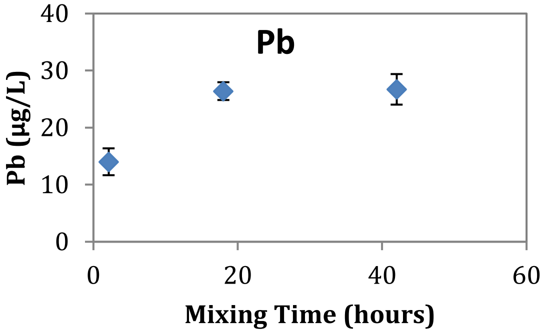

K
K (µg/L)
200
150
100
50
0
0
20
40
60
Mixing Time (hours)

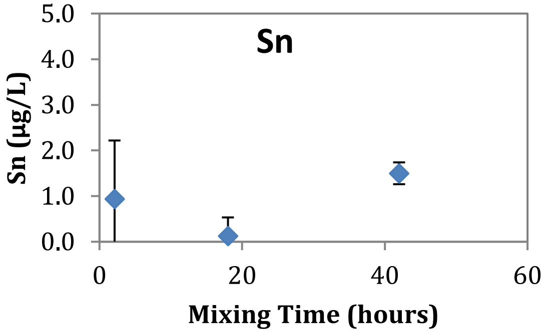

Mg
Mg (mg/L)
4.0
3.0
2.0
1.0
0.0
0
20
40
60
Mixing Time (hours)

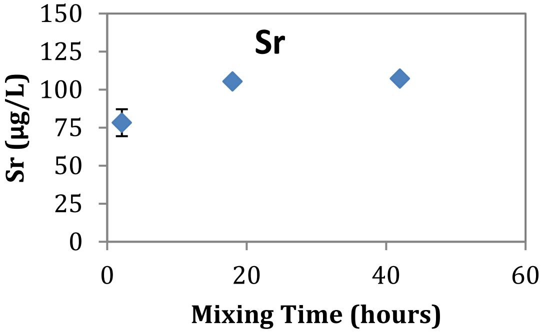

Mn
Mn (µg/L)
10.0
8.0
6.0
4.0
2.0
0.0
0
20
40
60
Mixing Time (hours)

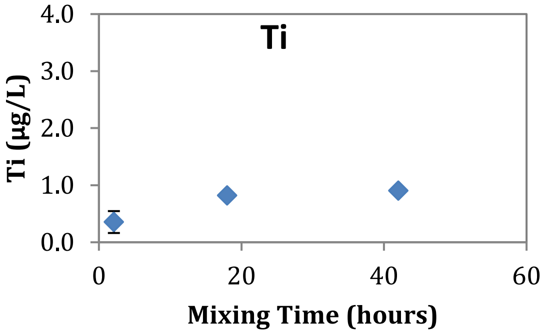

Na
Na (mg/L)
10.0
8.0
6.0
4.0
2.0
0.0
0
20
40
60
Mixing Time (hours)

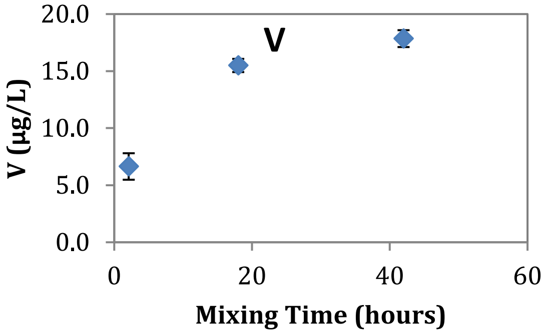

P
P (mg/L)
2.0
1.5
1.0
0.5
0.0
0
20
40
60
Mixing Time (hours)

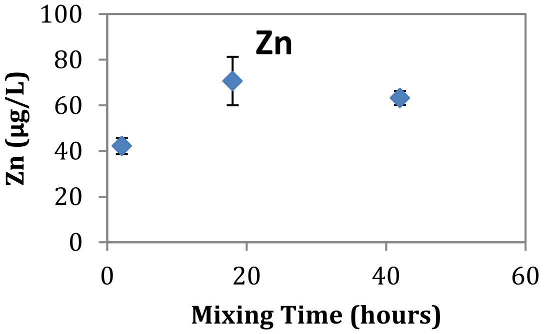

Pb
Pb (µg/L)
40
30
20
10
0
0
20
40
60
Mixing Time (hours)


Sn
Sn (µg/L)
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
Mixing Time (hours)


Sr
Sr (µg/L)
150
125
100
75
50
25
0
0
20
40
60
Mixing Time (hours)

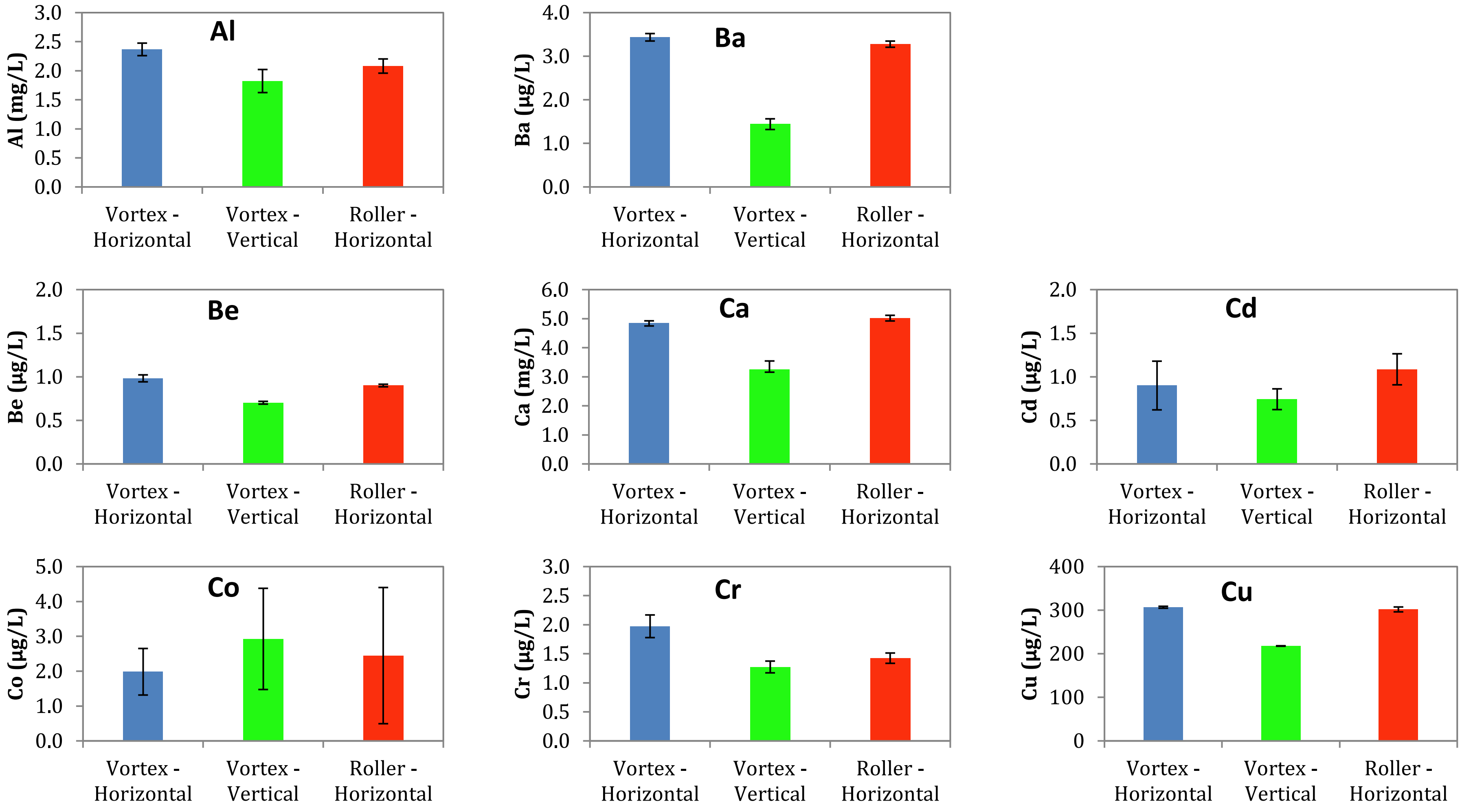

Ti
Ti (µg/L)
4.0
3.0
2.0
1.0
0.0
0
20
40
60
Mixing Time (hours)

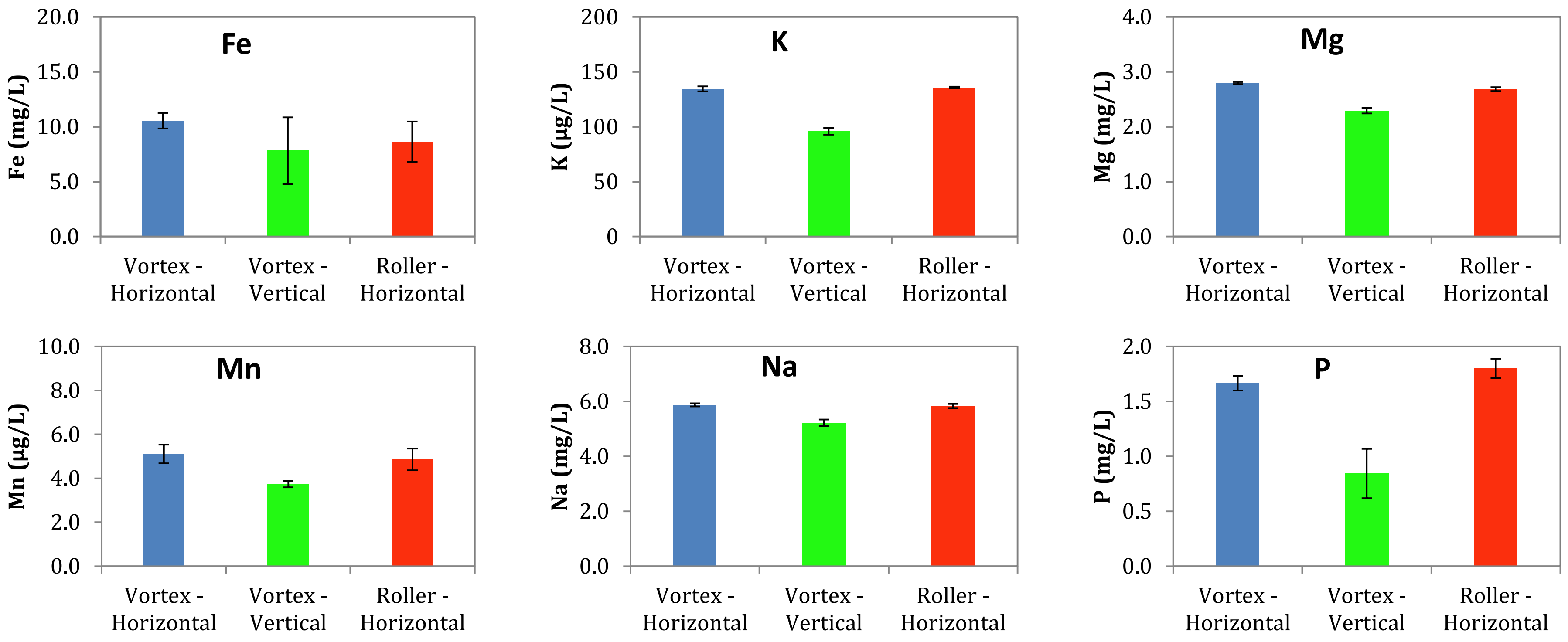

V
V (µg/L)
20.0
15.0
10.0
5.0
0.0
0
20
40
60
Mixing Time (hours)

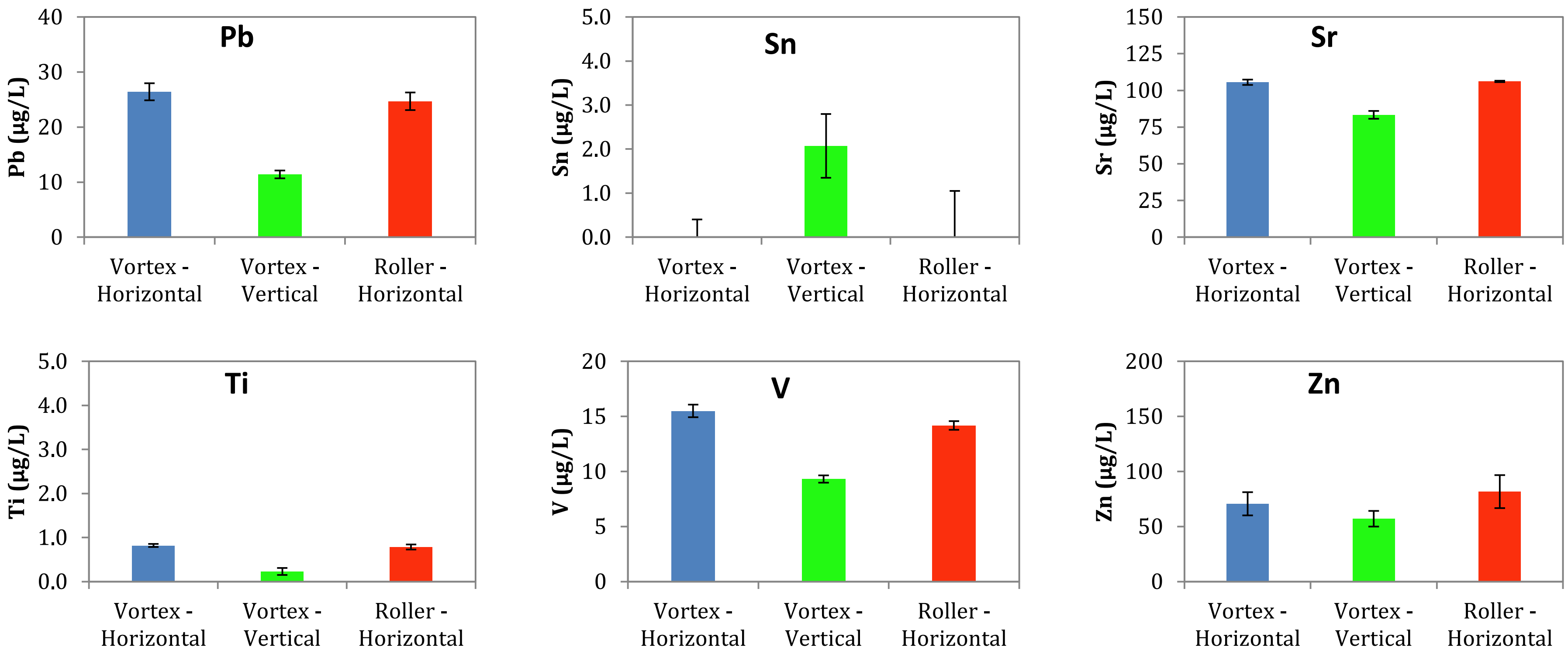

Zn
Zn (µg/L)
100
80
60
40
20
0
0
20
40
60
Mixing Time (hours)

Optimisation of leach test – mixing method

Leach test optimisation: effect of mixing method on trace element release from coal (error bars are ± one standard deviation).




Fe
Fe (mg/L)
20.0
15.0
10.0
5.0
0.0
K
K (µg/L)
200
150
100
50
0
Mg
Mg (mg/L)
4.0
3.0
2.0
1.0
0.0
Mn
Mn (µg/L)
10.0
8.0
6.0
4.0
2.0
0.0
Na
Na (mg/L)
8.0
6.0
4.0
2.0
0.0
P
P (mg/L)
2.0
1.5
1.0
0.5
0.0
Vortex - Horizontal
Vortex - Vertical
Roller - Horizontal


Pb
Pb (µg/L)
0
10
20
30
40
Sn
Sn (µg/L)
0.0
1.0
2.0
3.0
4.0
5.0
Sr
Sr (µg/L)
0
25
50
75
100
125
150
Ti
Ti (µg/L)
0.0
1.0
2.0
3.0
4.0
5.0
V
V (µg/L)
0
5
10
15
20
Zn
Zn (µg/L)
0
50
100
150
200
Vortex - Horizontal
Vortex - Vertical
Roller - Horizontal

Appendix B - Trace element analysis quality control data

Table B.1 Total Trace Element Recovery from SARM-18 Certified Coal Reference Material

	Units	**SARM-18 analysed mean (n=9)**	**SARM-18 Certified Value**	**SARM-18 Recovery (%)**
Al_2O_3	%	2.38	2.57	93
Ba	µg/g	74	78	94
Be	µg/g	4	4.1	97
CaO	%	0.17	0.18	95
Ce	µg/g	22	22	100
Cr	µg/g	17	16	104
Co	µg/g	7.1	6.7	106
Cu	µg/g	6.2	5.9	106
Eu	µg/g	0.34	0.3	115
Fe_2O_3	%	0.28	0.29	95
La	µg/g	10	10	100
Li	µg/g	10	11	92
MgO	%	0.11	0.11	96
Mn	µg/g	22	22	101
Ni	µg/g	12	11	108
P	µg/g	33	30	110
K_2O	%	0.12	0.15	83
Rb	µg/g	8.3	8.1	103
Sm	µg/g	1.9	2	94
Sc	µg/g	4.7	4.3	109
Sr	µg/g	46	44	104
S	%	0.57	0.56	102
Tb	µg/g	0.3	0.3	105
Th	µg/g	3.6	3.4	106
U	µg/g	1.8	1.5	122
V	µg/g	24	23	104

	Units	SARM-18 analysed mean (n=9)	SARM-18 Certified Value	SARM-18 Recovery (%)
Zn	µg/g	6	5.5	109
Zr	µg/g	63	67	94

Table B.2 Detection limits for the various trace elemental analyses conducted

Element	Units	0.01 M HCl leach	pH 5 citrate leach	pH 7 citrate leach	pH 7 no citrate leach	High pressure leach
Al	µg/L	10	2	2	0.3	10
Sb	µg/L	0.01	0.1	0.2	0.1	2
As	µg/L	0.02	1	3	1	2
Ba	µg/L	1	0.2	0.4	4	5
Be	µg/L	0.01	0.02	0.1	0.01	1
Bi	µg/L	0.01	0.04	0.04	0.05	2
B	µg/L	0.2	2	2	1	1
Cd	µg/L	0.01	0.4	0.4	0.2	2
Cs	µg/L	0.3	0.04	0.1	0.02	1
Ca	mg/L	0.1	0.2	0.3	0.1	0.1
Ce	µg/L	0.01	0.05	0.01	0.01	2
Cr	µg/L	0.1	1	0.5	1	1
Co	µg/L	0.01	0.1	0.3	0.04	2
Cu	µg/L	0.1	0.5	1	0.1	3
Dy	µg/L	0.01	0.02	0.03	0.02	0.01
Er	µg/L	0.001	0.01	0.01	0.02	0.02
Eu	µg/L	0.001	0.01	0.03	0.01	0.01
Gd	µg/L	0.001	0.02	0.03	0.1	0.1
Ga	µg/L	0.003	0.04	0.02	0.03	1
Au	µg/L	-	0.5	1	0.5	-
Hf	µg/L	0.01	0.1	0.4	0.1	0.2
Ho	µg/L	0.01	0.1	0.01	0.03	0.02
In	µg/L	0.02	0.04	0.05	0.05	2
Ir	µg/L	0.01	0.1	0.1	0.1	1
Fe	mg/L	0.04	0.02	0.1	0.1	0.1

Element	Units	0.01 M HCl leach	pH 5 citrate leach	pH 7 citrate leach	pH 7 no citrate leach	High pressure leach
La	µg/L	0.002	0.01	0.01	0.01	0.03
Pb	µg/L	1	0.3	0.04	0.1	1
Li	µg/L	0.1	0.1	0.01	0.03	1
Lu	µg/L	0.01	0.01	0.02	0.02	0.03
Mg	mg/L	0.1	0.1	0.2	0.1	0.1
Mn	mg/L	0.001	0.001	0.004	0.001	0.001
Mo	µg/L	0.01	0.1	0.3	0.2	1
Nd	µg/L	0.002	0.02	0.1	0.04	0.1
Ni	µg/L	0.1	0.5	1	1	2
Nb	µg/L	0.002	0.03	0.04	0.02	0.4
Os	µg/L	0.02	0.05	1	0.03	0.1
Pd	µg/L	-	0.1	0.1	0.1	1
P	µg/L	1	1	3	2	-
Pt	µg/L	-	0.2	0.2	0.2	1
K	mg/L	0.01	0.03	0.1	0.02	0.1
Rh	µg/L	0.01	0.1	0.1	0.2	0.1
Rb	µg/L	0.01	0.02	0.03	0.05	0.1
Ru	µg/L	0.01	0.04	0.2	0.1	0.1
Sm	µg/L	0.05	0.1	0.04	0.03	0.04
Sc	µg/L	0.1	2	2	1	1
Se	µg/L	0.1	0.1	0.2	1	1
Ag	µg/L	0.01	0.1	0.2	0.2	5
Sr	mg/L	0.001	0.1	0.03	0.2	2
S	mg/L	0.01	1	2	0.5	-
Ta	µg/L	0.001	0.02	0.04	0.01	0.1
Te	µg/L	0.02	1	1	1	1
Tb	µg/L	0.001	0.01	0.01	0.01	0.004
Tl	µg/L	0.01	0.1	0.3	0.1	1
Th	µg/L	0.001	0.01	0.03	0.01	0.03
Tm	µg/L	0.001	0.01	0.02	0.01	0.01
Sn	µg/L	0.01	0.04	0.1	0.2	1
Ti	µg/L	0.1	0.1	0.2	0.1	10
W	µg/L	0.01	0.1	0.5	0.04	0.1

Element	Units	0.01 M HCl leach	pH 5 citrate leach	pH 7 citrate leach	pH 7 no citrate leach	High pressure leach
U	µg/L	0.01	0.01	0.01	0.01	1
V	µg/L	0.04	0.1	0.5	1	1
Yb	µg/L	0.001	0.01	0.02	0.01	0.01
Zn	µg/L	0.1	0.1	0.1	0.2	10
Zr	µg/L	0.02	0.2	1	0.2	0.2
Y	µg/L	-	-	-	-	0.03
Hg	µg/L	0.004	-	-	-	1
Pr	µg/L	-	-	-	-	0.01
Re	µg/L	-	-	-	-	0.02

Table B.3 Trace elements in coal samples: limit of detection

Element	Units	LOD	Element	Units	LOD
Al	µg/g	200	Ni	µg/g	0.2
Sb	µg/g	0.004	Nb	µg/g	0.03
As	µg/g	0.2	Os	µg/g	0.01
Ba	µg/g	0.2	Pd	µg/g	-
Be	µg/g	0.005	P	µg/g	20
Bi	µg/g	0.004	Pt	µg/g	0.005
B	µg/g	0.4	K	µg/g	8
Cd	µg/g	0.01	Rh	µg/g	0.01
Cs	µg/g	0.03	Rb	µg/g	0.1
Ca	µg/g	4	Ru	µg/g	0.01
Ce	µg/g	0.1	Sm	µg/g	0.003
Cr	µg/g	0.2	Sc	µg/g	0.02
Co	µg/g	0.005	Se	µg/g	0.01
Cu	µg/g	0.03	Ag	µg/g	0.02
Dy	µg/g	0.005	Sr	µg/g	0.2
Er	µg/g	0.005	S	µg/g	70
Eu	µg/g	0.001	Ta	µg/g	0.01
Gd	µg/g	0.004	Te	µg/g	0.01
Ga	µg/g	0.02	Tb	µg/g	0.001
Au	µg/g	-	Tl	µg/g	0.01
Hf	µg/g	0.01	Th	µg/g	0.02
Ho	µg/g	0.002	Tm	µg/g	0.0003
In	µg/g	0.003	Sn	µg/g	0.05
Ir	µg/g	0.03	Ti	µg/g	8
Fe	µg/g	6	W	µg/g	0.01
La	µg/g	0.05	U	µg/g	0.002
Pb	µg/g	0.1	V	µg/g	0.1
Li	µg/g	0.04	Yb	µg/g	0.0003
Lu	µg/g	0.002	Zn	µg/g	0.2
Mg	µg/g	6	Zr	µg/g	0.3
Mn	µg/g	0.2			
Mo	µg/g	0.01			
Nd	µg/g	0.04			

Appendix C - Organic analysis data

Table C.1 List of target organic compounds measured using GC-MS/MS techniques

Chemical (CAS number)	**Chemical class**	**Log K_{ow}[a,c]**	**S [b,c] (mg/L)**	**Ions used in SIM (m/z)**
Acenaphthylene (208-96-8)	PAH	3.94	16.1	152,151,76
Acenaphthene (83-32-9)	PAH	3.92	3.9	154,153,76
Anthracene (120-12-7)	PAH	4.45	0.04	179,178,176,152,89
Benzo[a]anthracene (56-55-3)	PAH	5.76	0.009	228,226,114,113
Benzo[a]pyrene (50-32-8)	PAH	6.13	0.002	252,250,126
Benzo[b,k]fluoranthene (205-99-2, 207-08-9)	PAH	5.78,6.11	0.0015,0.0008	252,250,126
Benzo[g,h,i]perylene (191-24-2)	PAH	6.63	0.0003	277,276,274,207,138
Benzoic acid (65-85-0)	Organic acid	1.87	3400	122,105,77
Chrysene (218-01-9)	PAH	5.81	0.002	228,226,114,113
Dibenzo[a,h]anthracene (53-70-3)	PAH	6.75	0.002	278,139
2,3-Dimethylnaphthalene* (581-40-8)	PAH	4.4	1.99	155,140,127
2,4-Dimethylphenol (xylenol) (105-67-9)	Phenol	2.3	7870	107,91
4-Ethylphenol* (123-07-9)	Phenol	2.58	4900	121,106,76
Fluoranthene (206-44-0)	PAH	5.16	0.26	202,200,101
Fluorene (86-73-7)	PAH	4.18	1.69	166,165,82
4-Isopropylphenol* (99-89-8)	Phenol	2.9	1102	135,120

Chemical **(CAS number)**	**Chemical class**	**Log K_{ow} [a,c]**	**S [b,c]** **(mg/L)**	**Ions used in SIM** **(m/z)**
1-and 2-Methylnaphthalene* (90-12-0, 91-57-6)	PAH	3.87	26	141,125,114
o,p-Methylphenol (cresol) (95-48-7, 106-44-5)	Phenol	1.95	25900	108,107,90,79,77
Naphthalene (91-20-3)	PAH	3.3	31	128,127,102,51
Phenol (108-95-2)	Phenol	1.46	82800	94,66,65
2-Phenylacetophenone* (451-40-1)	Acetophenone	3.18	88	104,90,76
1-Phenylnaphthalene* (605-02-7)	PAH	4.93	2.8	178,152,104
4-Phenylphenol* (92-69-3)	Phenol	3.2	56	169,140,114
Pyrene (129-00-0)	PAH	4.88	0.13	202,200,101

**not included in preliminary study; [a]octanol-water partition coefficient, [b]water solubility [c]data obtained from SRC FatePointer PhysProp Database (http://esc.srcinc.com/fatepointer/search.asp) dusing targeted GC-MS/MS analysis (83-32-()*

Table C.2 Concentrations and recoveries (%) of organic analytes in spiked coal, relative to spiked sand (matrix effect) in organic solvent extracts

Compound	**LOR**	**Ethyl acetate/Methanol**		**Hexane/Acetone**	
		No Florisil®	**Florisil®**	**No Florisil®**	**Florisil®**
		Concentration (mg/kg) and (% recovery)			
Acenaphthylene	0.5	<LOR (205±37)	<LOR (109±70)	<LOR (89a)	<LOR (19a)
Acenaphthene	0.5	<LOR (235±39)	<LOR (123±75)	<LOR (93[a])	<LOR (47[a])
Anthracene	0.5	0.55±0.04 (1370±193)	1.05±0.08 (737±369)	2.32±0.07 (416±567)	2.98±1.18 (205±316)
Benzo[a]anthracene	0.5	0.1±0.05 (1402±326)	0.21±0.02 (631±328)	0.68±0.01 (174±270)	0.64±0.24 (178±288)
Benzo[a]pyrene	0.5	0.77±0.01 (330±8)	0.56±0.05 (393±71)	1.55±0.09 (134±210)	1.42±0.56 (134±222)
Benzo[b,k]fluoranthene	0.5	0.1±0.01 (819±155)	0.29±0.02 (371±189)	0.91±0.05 (111±175)	0.99±0.38 (95±155)
Benzo[g,h,i]perylene	0.5	0.14±0.01 (653±37)	0.35±0.03 (292±171)	1.25±0.08 (77±117)	1.24±0.43 (68±110)
Benzoic acid	0.25	<LOR (2130±258)	<LOR (3037±1612)	<LOR (276±462)	0.66±0.02 (22±32)
Chrysene	0.5	0.36±0.01 (1478±117)	0.65±0.09 (747±390)	2.12±0.07 (220±317)	2.1±0.92 (195±310)
Dibenzo[a,h]anthracene	0.5	0.2±0.01 (652±43)	0.36±0.03 (287±169)	1.35±0.1 (74±112)	1.32±0.46 (65±105)
Dimethylphenol	0.1	23.2±7.1 (30±7)	8.14±0.58 (100±60)	5.01±0.4 (100±171)	26.3±21 (17±22)
Fluoranthene	0.5	11.7±2.4 (23±12)	2.22±0.27 (9±1)	3.8±1.29 (8±9)	112±54 (5±6)
Fluorene	0.5	0.23±0.03 (1104±198)	0.41±0.01 (696±406)	0.33±0.02 (522±865)	1.27±0.7 (134±225)
o,p-Methylphenol	0.1	<LOR (3104±115)	<LOR (3200±3028)	<LOR (788±449)	<LOR (9±13)
Naphthalene	0.1	<LOR (173±15)	<LOR (1983±2226)	<LOR (-[b])	<LOR (2±4)
Phenol	0.1	<LOR (99±5)	<LOR (-)	<LOR (-)	<LOR (-)
Pyrene	0.5	0.1±0.01	0.19±0.02	0.82±0.04	0.64±0.27

Compound	**LOR**	**Ethyl acetate/Methanol**		**Hexane/Acetone**	
		No Florisil®	**Florisil®**	**No Florisil®**	**Florisil®**
		Concentration (mg/kg) and (% recovery)			
		(1430±287)	(668±321)	(211±328)	(176±288)

[a] only one replicate quantifiable; [b] recovery not quantifiable

Table C.3 Summary of major analytes detected in synthetic groundwater leachate extracts using a NIST library search

Chemical (CAS number)	Chemical class	Sand blank	Narrabri	Carsborough Downs	Oaky Creek	Blackwater	New Acland	Wandoan 2009	Wandoan 2011	Gallilee
1,1-dimethylcyclohexane (590-66-9)	alkane	-	-	✓	-	✓	-	✓	-	-
1-ethyl-2-methyl cyclohexane (4923-78-8)	alkane	-	-	-	-	-	-	-	✓	-
heptadecane (629-78-7)	alkane	-	-	✓	-	✓	-	-	-	✓
3-methyl buten-2-al (107-86-8)	aldehyde	-	-	-	-	-	-	-	✓	✓
(1-methylhexylidene) methylamine (22058-71-5)	methylamine	-	-	✓	-	✓	-	-	-	-
1-methyl-7-(methylethyl)phenanthrene (483-65-8)	PAH	-	✓	-	-	-	-	-	-	-
methylnonadecane	alkane	-	-	-	-	✓	-	-	-	-
1-methyl-2-propyl cyclohexane (4291-79-6)	alkane	-	-	-	✓	-	✓	-	-	-
nonadecane (629-92-5)	alkane	-	✓	-	-	-	-	-	-	✓
octacosane	alkane	-	-	-	✓	-	-	-	-	-

Chemical (CAS number)	Chemical class	Sand blank	Narrabri	Carsborough Downs	Oaky Creek	Blackwater	New Acland	Wandoan 2009	Wandoan 2011	Gallilee
(630-02-4)										
1,2,3,4,5-pentamethylcyclopentane (33189-46-7)	alkane	-	✓	✓	-	-	-	✓	-	-
propylcyclopentanone	ketone	-	-	-	✓	✓	-	-	-	-
tetradecane (629-59-4)	alkane	-	-	✓	-	✓	-	-	-	-
tetramethyl-5-dicynediol (NA)	alcohol	-	✓	✓	-	✓	✓	✓	✓	✓
4,4,6-trimethylcyclohexen-1-ol (21592-95-0)	alkane	-	-	✓	-	✓	-	✓	✓	-

Table C.4 Summary of major analytes detected in synthetic groundwater and hydraulic fracturing fluid leachate extracts using a NIST library search

Chemical (CAS number)	**Chemical class**	**Sand blank**	**Narrabri**	**Carsborough Downs**	**Oaky Creek**	**Blackwater**	**New Acland**	**Wandoan 2009**	**Wandoan 2011**	**Gallilee**
butoxyethanol * (111-76-2)	ether alcohol	✓	✓	✓	✓	✓	✓	✓	✓	✓
cis-carveol * (2102-59-2)	monoterpene	✓	✓	✓	✓	✓	✓	✓	✓	✓
trans-carveol * (1197-07-5)	monoterpene	✓	✓	✓	✓	✓	✓	✓	✓	✓
carvone * (6485-40-1)	monoterpene	✓	✓	✓	✓	✓	✓	✓	✓	✓
2-cyclohexen-1-one 4-(1-methylethenyl) * (62702-87-8)	cyclic enone	✓	-	-	-	-	-	-	-	-
3,3,5-trimethyl cyclohexenone (78-59-1)	cyclic enone	-	-	✓	✓	-	-	✓	-	-
dodecyl acrylate (2156-97-0)	acrylate ester	-	-	-	✓	-	-	-	-	-
2-ethyl-2-hexenal * (645-62-5)	aldehyde	✓	-	-	-	-	-	-	-	-
2-ethyl-2-hexenol * (50639-00-4)	alkyl alcohol	✓	✓	✓	✓	✓	✓	✓	✓	✓
hexadecanoic acid * (57-10-3)	fatty acid	✓	✓	✓	✓	-	✓	✓	✓	✓

Chemical **(CAS number)**	**Chemical class**	**Sand blank**	**Narrabri**	**Carsborough Downs**	**Oaky Creek**	**Blackwater**	**New Acland**	**Wandoan 2009**	**Wandoan 2011**	**Gallilee**
hexadecyl acrlyate (13402-02-3)	acrylate ester	-	✓	-	-	-	-	-	-	-
limonene (138-86-3)	monoterpene	✓	-	-	-	-	-	-	-	-
limonene glycol (1946-00-5)	monoterpene	-	✓	✓	✓	-	-	-	-	-
limonene oxide (13837-75-7)	monoterpene	✓	-	-	-	-	-	-	-	-
linalool * (78-70-6)	monoterpene	✓	✓	✓	✓	✓	✓	✓	✓	✓
linalool oxide * (5989-33-3)	monoterpene	✓	✓	✓	✓	✓	✓	✓	✓	✓
mentha-1,8-dienol * (2102-62-7)	monoterpene	✓	✓	✓	✓	✓	✓	✓	✓	✓
4-methyl 2,3-dihydro furan (34314-83-5)	heterocycle	-	-	✓	-	-	-	✓	-	✓
methylbenzene (108-88-3)	substituted benzene	-	-	-	✓	-	-	-	-	-
2-methyl-2-(3-methyl-1-vinyl-2-butenyl)oxirane		-	-	-	✓	-	-	-	-	-
octadecane (593-45-3)	alkane	-	✓	✓	-	-	-	-	-	-

Chemical (CAS number)	Chemical class	Sand blank	Narrabri	Carsborough Downs	Oaky Creek	Blackwater	New Acland	Wandoan 2009	Wandoan 2011	Gallilee
nootkatone * (4674-50-4)	sesquiterpene	✓	-	✓	-	✓	-	-	-	-
octadecanoic acid (112-61-8)	fatty acid	✓	-	-	-	-	-	-	-	-
terpinene (99-86-5)	monoterpene	-	-	-	-	-	-	✓	-	-
tetracontane (7098-22-8)	alkane	-	✓	-	-	-	-	-	-	-
verbenol (473-67-6)	monterpene							✓		

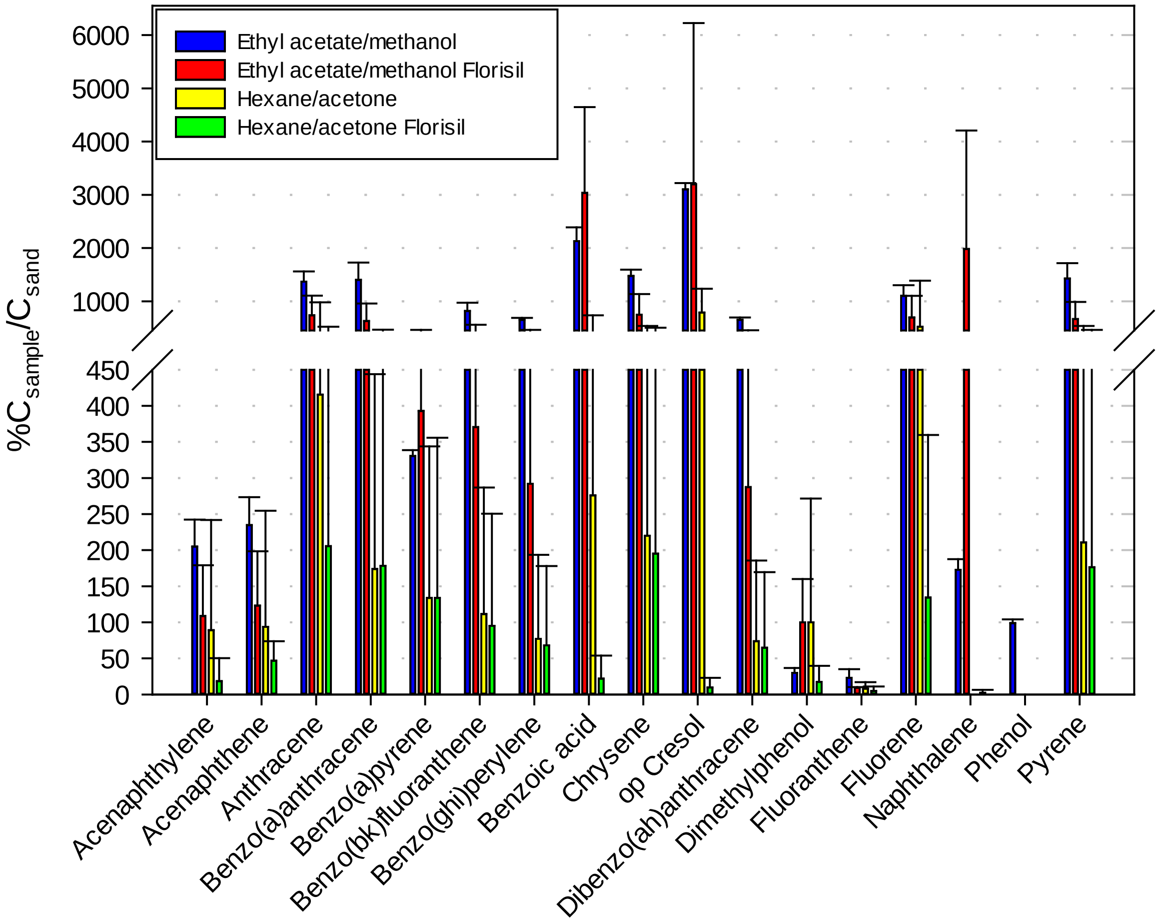
**detected in both sand blank and coal leachates*

Table C.5 Summary of mean concentrations (±S.D.) of phenols detected in leachates with synthetic groundwater from eight coals (concentrations are in µg/L)

Compound	**LOR**	**Narrabri**	**Carsborough Downs**	**Oaky Creek**	**Blackwater**	**New Acland**	**Wandoan 2009**	**Wandoan 2011**	**Gallilee**
Phenol	10	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
2-Methylphenol	10	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
3-and 4-Methylphenols	20	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
2,4-Dimethyphenol	10	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR

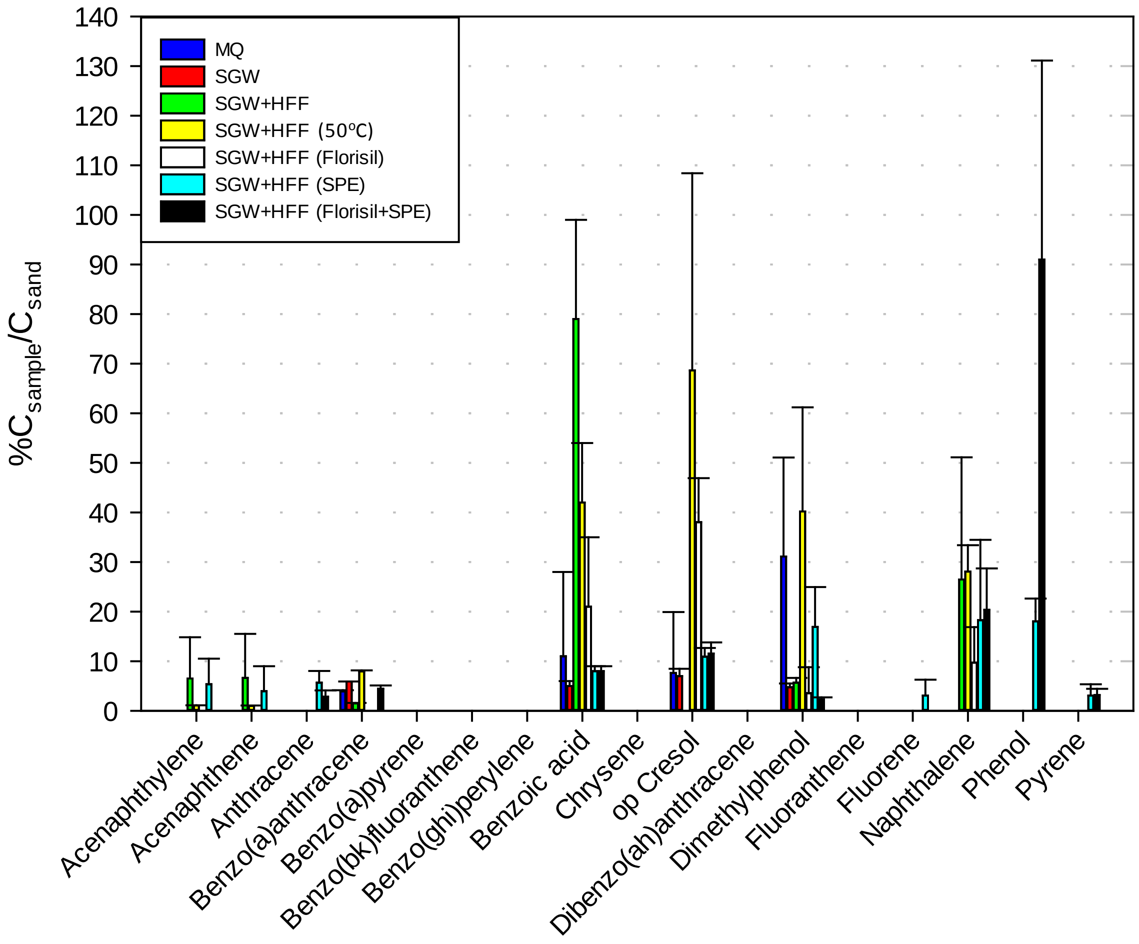
Table C.6 Summary of mean concentrations (±S.D.) of phenols detected in leachates with synthetic groundwater + hydraulic fracturing fluid chemicals from eight coals (concentrations are in µg/L)

Compound	**LOR**	**Narrabri**	**Carsborough Downs**	**Oaky Creek**	**Blackwater**	**New Acland**	**Wandoan 2009**	**Wandoan 2011**	**Gallilee**
Phenol	> 10	273 (±76)	237 (±70)	165 (±134)	346 (±140)	190 (±95)	213 (±105)	135 (±161)	205 (±166)
2-Chlorophenol	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10
2-Methylphenol	> 10	23 (±10)	22 (±8)	25 (±10)	28 (±7)	20 (±4)	19 (±7)	23 (±15)	22 (±6)
3-and 4-Methylphenols	> 20	83 (±33)	78 (±7)	104 (±33)	95 (±23)	63 (±14)	76 (±21)	68 (±60)	73 (±3)
2,4-Dimethyphenol	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10	> 10



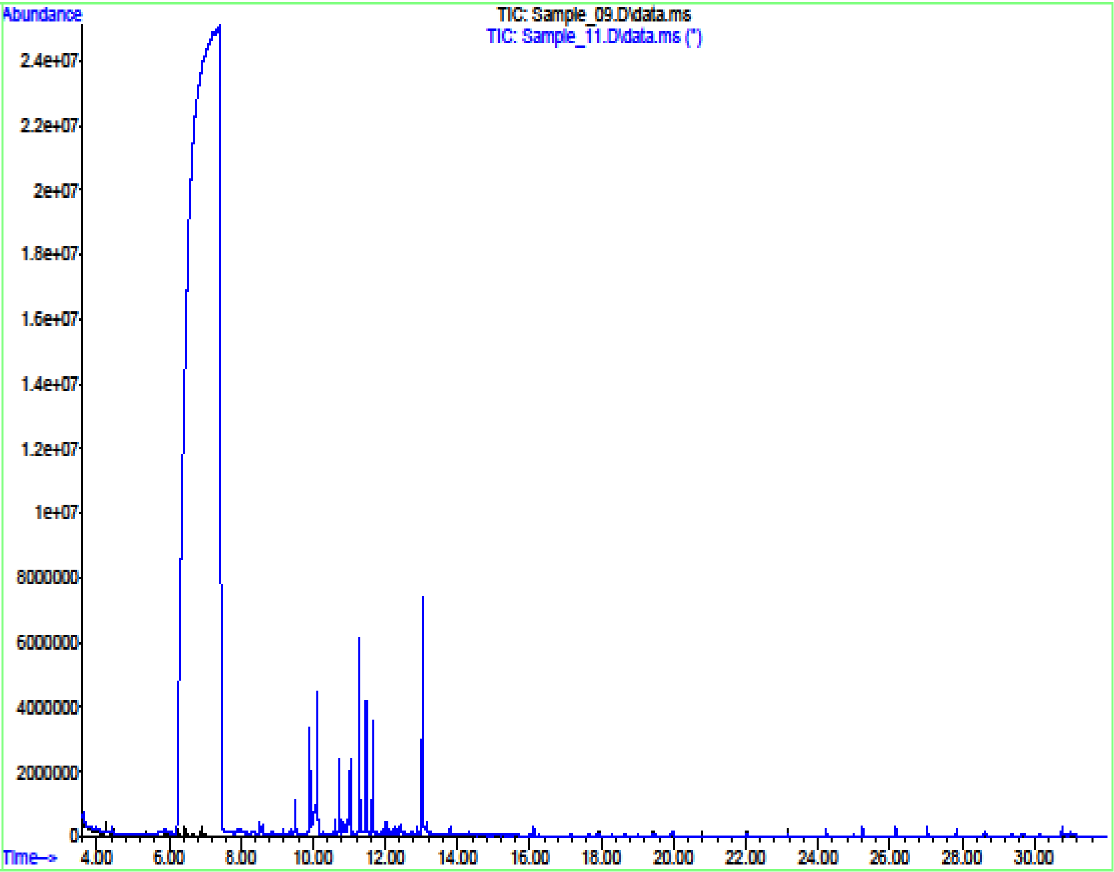
Florisil® was used to clean up the leachates. The coal was spiked with organic compounds and compared with matrix free sand using various solvents

Figure C.1 The matrix effect and recovery efficiency measured as a relative response (compared to the sand control) of PAHs and phenols leached from coal with organic solvents under high pressure (10.3 kPa) and temperature (100°C)



The aqueous solutions were high purity water (Milli-Q), synthetic ground water (SGW), and synthetic groundwater mixed with hydraulic fracturing fluid (SGW + HFF).

Figure C.2 The matrix effect and recovery efficiency measured as a relative response (compared to the sand control) of PAHs and phenols leached from spiked coal samples with aqueous solutions under high pressure (10.3 kPa) and temperature (100°C unless otherwise stated)



The intense peak at 7 minutes corresponds with butoxyethanol.

Figure C.3 Overlain GC-MS full scan (50-500 m/z) chromatogram of simulated groundwater (black line) and hydraulic fracturing fluid (blue line) leachates of Carsborough Downs coal