



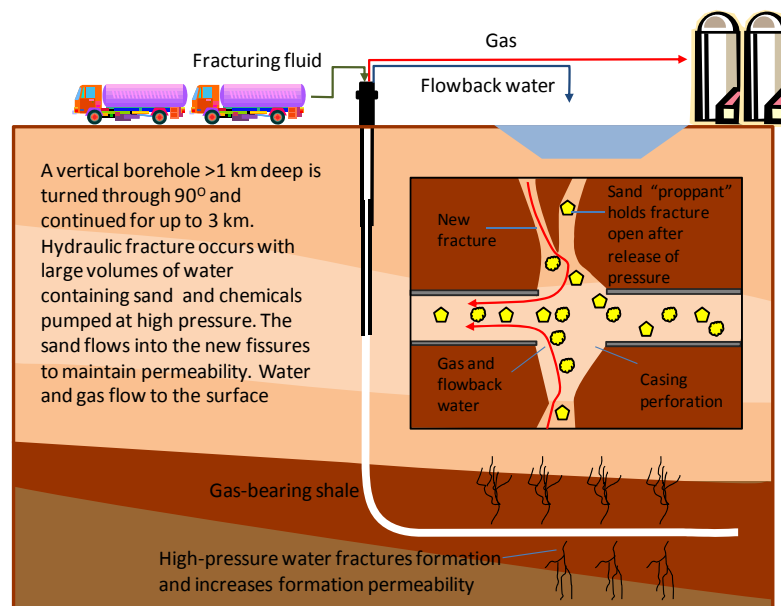
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Potential groundwater impact from exploitation of shale gas in the UK

Groundwater Science Programme

Open Report OR/12/001



BRITISH GEOLOGICAL SURVEY

GROUNDWATER SCIENCE PROGRAMME

OPEN REPORT OR/12/001

Potential groundwater impact from exploitation of shale gas in the UK

M E Stuart

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British Geological Survey offices

BGS Central Enquiries Desk

Tel 0115 936 3143 Fax 0115 936 3276
email enquiries@bgs.ac.uk

Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488
email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

Tel 0131 667 1000 Fax 0131 668 2683
email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090 Fax 020 7584 8270
Tel 020 7942 5344/45 email bgs_london@bgs.ac.uk

Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

Tel 029 2052 1962 Fax 029 2052 1963

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

Tel 028 9038 8462 Fax 028 9038 8461

www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500 Fax 01793 411501
www.nerc.ac.uk

Website www.bgs.ac.uk

Shop online at www.geologyshop.com

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Summary

This report is a desk study to evaluate the potential risks to groundwater in the UK from exploitation of shale gas. As yet there is little information for UK so we need to look to the USA experience for transferable information.

The UK may possess considerable reserves of shale gas. Significant areas include the Widmerpool Gulf, near Nottingham, and the Elsewrick field near Blackpool. Work has begun near Blackpool.

Hydraulic fracturing (“fracking”) in combination with horizontal drilling is an essential part of the shale gas production process and has been in use in the USA since about 1948. Extraction involved drilling of deep horizontal wells and enhancing the natural permeability of the shale by hydraulic fracturing. Fluid is introduced at a rate sufficient to raise the downhole pressure above the fracture pressure of the formation rock. The stress induced by the pressure creates fissures and interconnected cracks that increase the permeability of the formation and enable greater flow rates of gas into the well.

Groundwater may be potentially contaminated by extraction of shale gas both from the constituents of shale gas itself, from the formulation and deep injection of water containing a cocktail of additives used for hydraulic fracturing and from flowback water released during gas extraction which may have a high content of saline formation water. Shale gas is predominantly methane of thermogenic origin with low percentages of C₂ (ethane) and C₃ (propane) hydrocarbons. Its ¹³C isotopic signature allows it to be distinguished from shallow biogenic methane in the subsurface. Documented instances of groundwater contamination from the USA are all related to the leakage of methane into groundwater.

Fracking chemicals include hydrochloric acid, polyacrylamide, mineral oil, isopropanol, potassium chloride and ethylene glycol and low concentrations of pH buffers, corrosion inhibitors, biocides and gelling agents.

The large volumes of water required may also put pressure on groundwater resources with impacts on other uses and groundwater dependent ecosystems. Reuse of flowback water involves treatment to remove high TDS.

For UK we need to determine whether fields likely to be exploited for shale gas are overlain by significant aquifers. For aquifers at outcrop the vulnerability of groundwater to surface pollution from operations and flowback water can be informed by existing vulnerability mapping and other information. The vulnerability of groundwater to pollution from fracking operations and shale gas requires the determination of the relative depths of groundwater and shale gas reservoirs and the nature of the intervening strata.

1 Introduction

1.1 AIM OF REPORT

Demand for gas in the UK is steadily increasing, North Sea gas reserves are declining and the UK has become a net importer of gas. Shale gas drilling in the UK has been given the go-ahead by MPs in a report looking at the impact it could have on water supplies, energy security and greenhouse gas emissions (Energy and Climate Change Select Committee, 2011). In order to meet demand in the future, energy exploration may be focused on our 'unconventional' reservoirs, including shales (mudstones, claystones, and other fine-grained rocks).

Work towards extraction of shale gas began in the UK in August 2010 with the drilling of a 2700 m deep exploratory well to the Bowland Shale at Preese Hall, near Blackpool, NW England. The second phase involving hydraulic fracturing began in March 2011. Work was temporarily suspended on 1 June 2011 after a 1.5 magnitude earth quake was detected. Work began at a second site at Banks, near Southport on 22 August 2011 and at Grange Hill Farm.

The aim of this desk study is to evaluate what the potential risks to groundwater from exploitation of shale gas could be for the UK. As yet there is little information for UK so we need to look to the USA where this is a long-established technique, for transferable information.

In an assessment from the Tyndall Centre, Broderick et al. (2011) state that the potential for groundwater contamination is a key risk associated with shale gas extraction, although there is limited evidence. They cite that the US EPA has instigated a comprehensive research study into this issue and New York State has introduced a moratorium on any new wells.

1.2 SHALE GAS

Shale gas is natural gas entrapped in shale and is distinct from gas in other low-permeability reservoirs and from “conventional” gas (Gregory et al., 2011). Shales are fine-grained, clastic sedimentary rocks predominantly comprised of consolidated clay sized particles that were deposited as muds in low-energy depositional environments and may contain other minerals such as quartz, calcite, and pyrite. Deposited with these very fine-grained sediments is organic matter in the form of algae, plant, and animal derived organic debris (Arthur et al., 2009).

The shale formation is both the source and the reservoir for the natural gas, which is predominantly methane (~90%) but may also contain other hydrocarbons, carbon dioxide, nitrogen, hydrogen sulphide, and rare gases (Lapidus et al., 2000). The gas is held in natural fractures and pore spaces or adsorbed onto the organic material and minerals in the formation (Jenkins and Boyer, 2008).

Gas embedded in shale rock formations deep below the Earth's surface has long been considered inaccessible, due to high drilling costs and because shales lack sufficient natural permeability for the recovery of gas at rates suitable for large-scale production. Deep borings must be used and fractures must be engineered to enable commercial viability (Jenkins and Boyer, 2008). New horizontal drilling methods, combined with techniques to fracture the rock, have for the first time made shale gas production practical. New technology for gas production from shale formations evolved in the Barnett Shale in Texas, and its economic success has led to the rapid exploration of shale formations in many countries and has greatly increased the estimates of global natural gas reserves in the world. The areas of the world assessed for potential shale gas resources are shown in Figure 1.1.

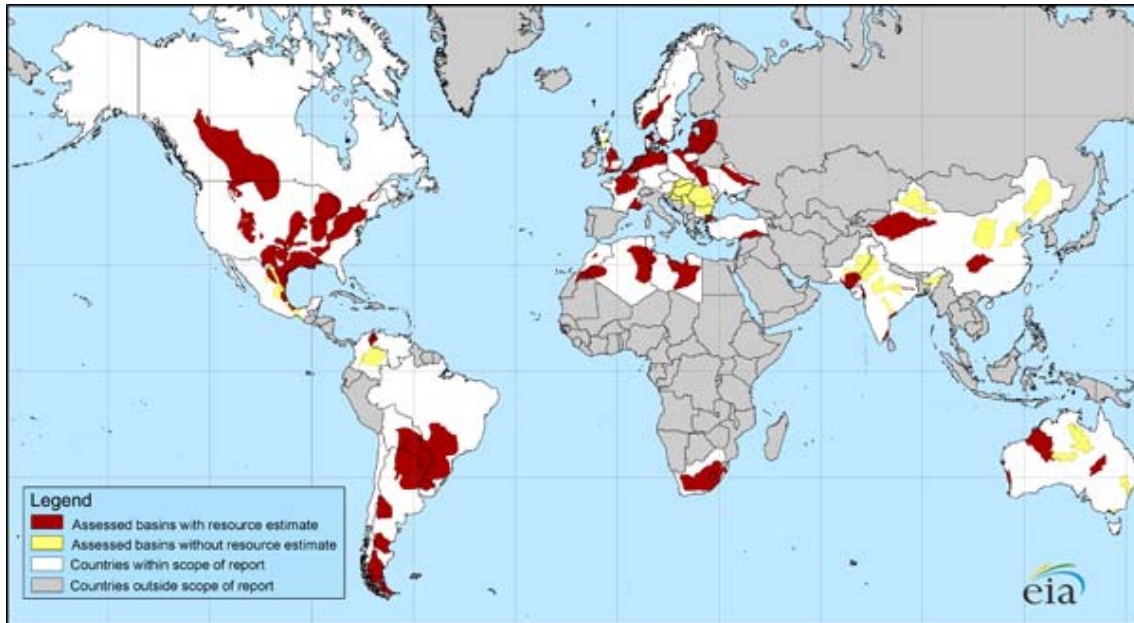


Figure 1.1 Map of world shale gas resources assessed by the US Energy Information Administration (EIA, 2011a)

1.3 EXTRACTION METHODS

Hydraulic fracturing (“fracking”) in combination with horizontal drilling is an essential part of the shale gas production process and has been in use since about 1948. Horizontal drilling greatly increases the length of contact between the shale gas formation and the wellbore relative to a conventional vertical well, and a single horizontal well may replace 3 or 4 vertical wells (Arthur et al., 2009; Gjelten, 2009). Decreasing the number of wells decreases production costs and environmental risks associated with site construction, drilling, and well development, and contributes to the economic feasibility of shale gas production.

Hydraulic fracturing is a formation stimulation practice used to create additional permeability in a producing formation (Arthur et al., 2009). By creating additional permeability the migration of fluids to the wellbore is facilitated. Hydraulic fracturing can be used to overcome barriers to the flow of fluids, one of the primary reasons development of gas shales has traditionally been limited. Barriers may include naturally low permeability common in shale formations or reduced permeability resulting from near wellbore permeability impairment caused during drilling activities.

Hydraulic fracturing involves the introduction of fluid at a rate sufficient to raise the downhole pressure above the fracture pressure of the formation rock. The stress induced by the pressure creates fissures and interconnected cracks that increase the permeability of the formation and enable greater flow rates of gas into the well. The process as typically used for shale gas development involves the pumping of sand-laden water into the target shale zone. Fluids pumped into the shale creates fractures or openings through which the sand flows, at the same time the sand acts to prop open the fractures that have been created. Once the pumping of fluids has stopped the sand remains in-place allowing fluids (both gas and water) to flow back to the wellbore. After hydraulic fracturing is performed, the pumping pressure is relieved and the fracture fluid returns to the surface through the well casing. This water is referred to as “flowback” (Figure 1.2).

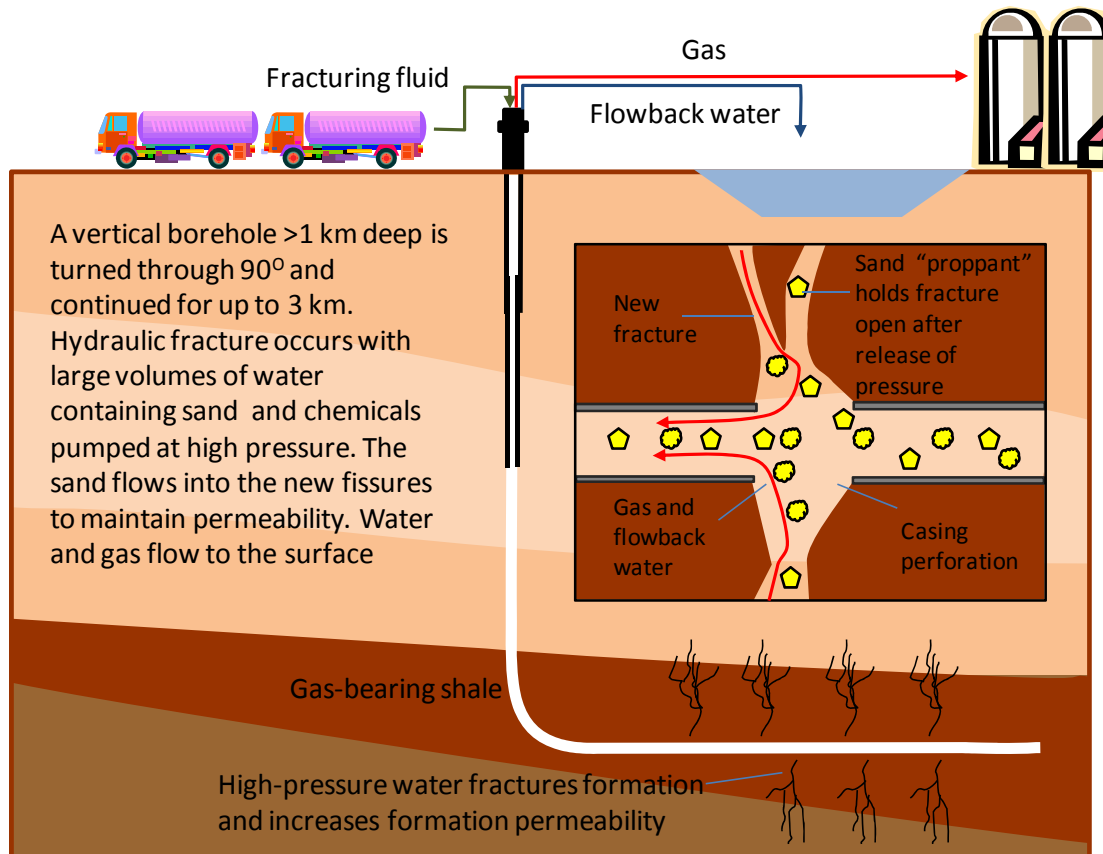


Figure 1.2 Hydraulic fracturing overview (adapted from Gregory et al., 2011)

Hydraulic fracturing of the horizontal shale gas wells is performed in stages (Arthur et al., 2009). Lateral lengths in typical shale gas development wells are from 300 m to more than 1500 m in length. Because of the length of exposed wellbore, it is usually not possible to maintain a downhole pressure sufficient to stimulate the entire length of a lateral in a single stimulation hydraulic fracture treatments of shale gas wells are performed by isolating portions of the lateral and performing multiple treatments to stimulate the entire length of the lateral portion of the well. The lifetime of an individual well may be only about 7 years (Wood et al., 2011).

1.4 USA

In the USA gas has been produced from shale in commercial quantities for nearly two centuries (Selley, 2005). The first commercial United States natural gas production (1821) came from an organic-rich Devonian shale in the Appalachian basin; wells were located and drilled with little appliance of science. (Curtis, 2002). Understanding the geological and geochemical nature of organic shale formations and improving their gas producibility have subsequently been the challenge of millions of dollars worth of research since the 1970s (Johnson and Doré, 2010). Harnessing this resource has become a multi-billion dollar international business, and has helped transform the North American market from gas starvation to guaranteed supply for 20 years or more. As with shale oil, shale gas systems are considered discrete, self enclosed systems in which the source, seal and reservoir are one and the same.

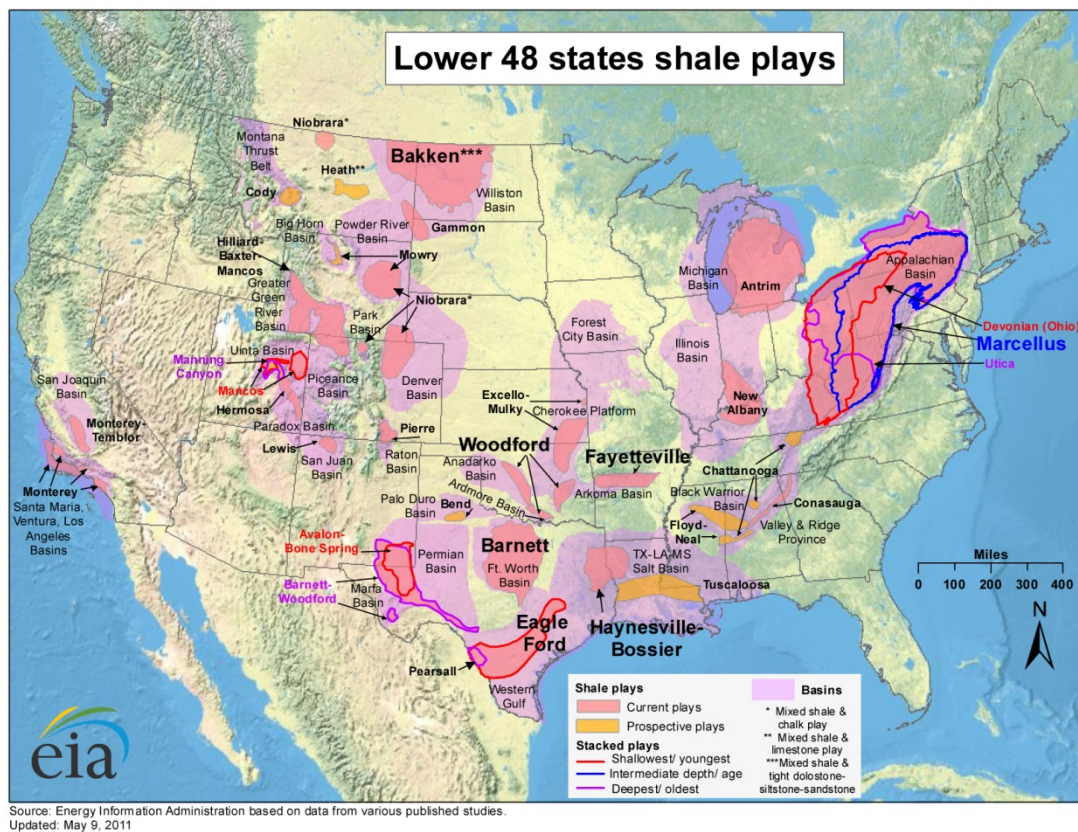


Figure 1.3 Locations of shale gas plays, USA (EIA, 2011b)

Production has been established in a range of major shale-gas systems or various geological ages (Figure 1.3), including:

- Antrim Shale, Michigan Basin (Devonian)
- Barnett Shale, Fort Worth Basin, Texas (Mississippian-Upper Carboniferous)
- Fayetteville Shale, Arkansas (Mississippian-Upper Carboniferous)
- Haynesville/Bossier Shale, Texas-Louisiana (Upper Jurassic)
- Lewis / Mancos Shale, San Juan Basin, New Mexico (Cretaceous)
- Marcellus Shale, Pennsylvania (Devonian)
- New Albany Shale, Illinois Basin, (Devonian/Mississippian)
- Ohio Shale, Appalachian Basin, (Devonian)
- Woodford Shale, Oklahoma (Devonian/Mississippian)

Technically recoverable natural gas from these shales is considered to be more than 1,744 trillion cubic feet (Tcf) (50 km^3), which includes 211 Tcf of proven reserves (Kargbo et al., 2010). At an annual production rate of about 19.3 Tcf, there is enough natural gas to supply the USA for the next 90 years with some estimates extending the supply to 116 years. The total number of natural gas and condensate wells in the USA rose 5.7% in 2008 to a record 478,562 (Kargbo et al., 2010).

The resource falls into two distinct types: biogenic and thermogenic, although there can also be mixtures of the two gas types (Johnson and Doré, 2010). Shale formations that presently produce gas commercially exhibit an unexpectedly wide variation in the values of five key parameters: thermal maturity (expressed as vitrinite reflectance), sorbed-gas fraction, reservoir thickness, total organic carbon content, and volume of gas in place. The degree of natural fracture development in an otherwise low-matrix-permeability shale reservoir is a controlling factor in gas producibility. To date, unstimulated commercial production has been achievable in only a small proportion of shale wells, those that intercept natural fracture networks. In most

other cases, a successful shale-gas well requires hydraulic stimulation. The current parameters used to assess shale gas prospectivity vary greatly and may not provide a strong predictive model. Consequently, additional criteria, such as the clay and mineral content of the shales, the burial history and the precise nature of the gas storage and retention systems are fertile grounds for further research.

1.5 POTENTIAL IN THE UK

Some 20 years ago it was suggested that, by analogy with the USA, the UK may possess considerable reserves of shale-gas. This was predicated on the assumption that shale-gas only resulted from the thermal maturation of organic-rich shales. Subsequently, it has been realized that shale-gas can be formed by methanogenic bacteria acting on organic-rich rocks, irrespective of age and thermal history, and especially as a result of post-glacial flushing of aquifers. This realization enhances British shale gas resources dramatically, making any fractured organic-rich shale prospective (Selley, 2005). Gas shows are commonly observed while drilling through shale stratigraphy, but there have been no Drill Stem Tests (DSTs) in the UK.

Potential British shale-gas petroleum systems include the thermally overmature Caledonide fold belt, the Lower Carboniferous thermally mature basinal shales of northern England and the Midland Valley of Scotland. The Jurassic (Lias, Oxford and Kimmeridge) clays may have considerable potential for thermogenic and biogenic shale-gas. The leaner Lower Cretaceous (Wealden) and Eocene (London Clay) formations of southern England may have minor potential for biogenic shale-gas (Selley, 2005).

Smith et al. (2010) assessed the potential targets as ranging in age from Cambrian to the late Jurassic, within the main UK organic-rich black shales: younger shales have been excluded because they have not reached the gas window, but they may possess a biogenic gas play (Figure 1.4 and Figure 1.5). A geographic information system, showing the distribution of potential reservoir units, has been created combining information on hydrocarbon shows, thermal maturity, fracture orientation, gas composition, and isotope data to identify potentially prospective areas for shale gas. The prospects include Lower Palaeozoic shale basins on the Midland Microcraton (a high risk because no conventional gas has been proved in this play), Lower Carboniferous shales in the Pennine Basin (the best prospect associated with conventional fields and high maturity), Carboniferous shales in the Stainmore and Northumberland Basin system (high risk because no conventional gas discoveries exist) and Jurassic shales in Wessex and Weald basins (small conventional fields signify potential here).

The UK has abundant shales at depth, although their distribution is not well known. The 2010 BGS/DECC Shale Gas report identified significant potential areas in northern England, including the Widmerpool Gulf near Nottingham and a large area centred on the Elsewicks Gas field, near Blackpool. The recently published UK data and analysis for shale gas prospectivity covers work up to March 2009 and identifies high prospect areas.

The UK shale gas industry is in its infancy and there are no reliable indicators of potential productivity. However, by analogy with similar producing shale gas plays in America, the UK shale gas reserve potential could be as large as 150 billion cubic metres (bcm) — very large compared with the 2–6 bcm estimate of undiscovered gas resources for onshore conventional petroleum (see BGS/DECC Shale Gas report)

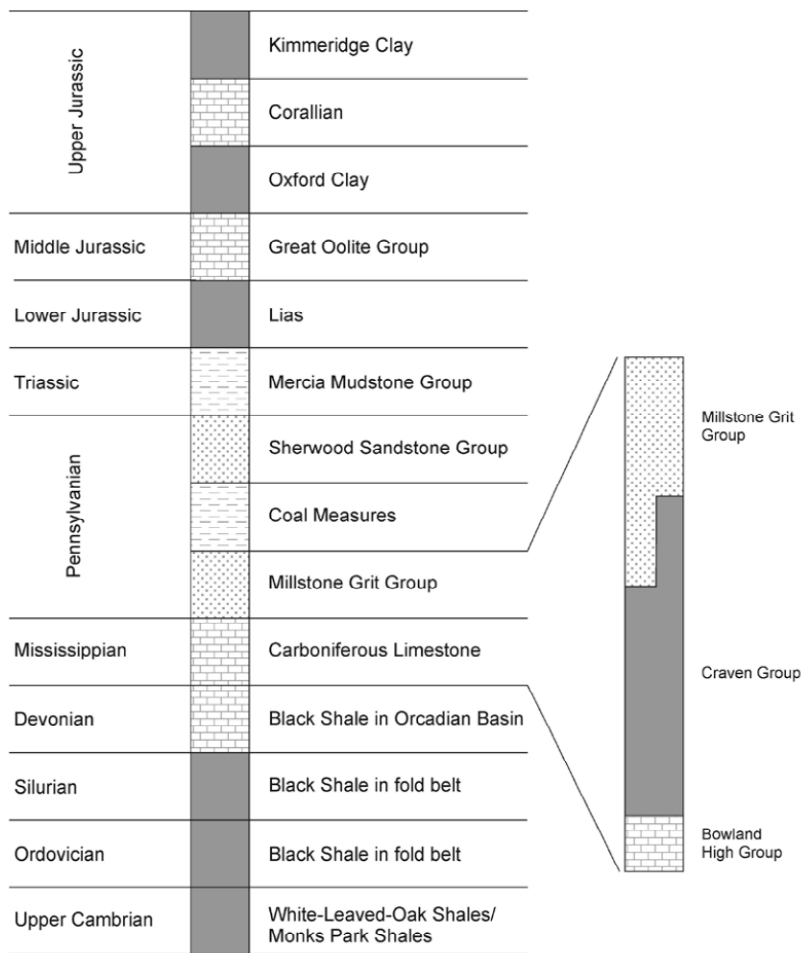


Figure 1.4 Main black shale formations in the UK with US classifications in left column (Smith et al., 2010)

1.6 CONCERNS

There are a range of web-based current affairs articles which detail popular concern on groundwater issues related to shale gas exploitation. These primarily address two areas:

- Contamination of water by chemicals added during the hydraulic fracturing process, such as benzene (Gjelten, 2009)
- Contamination of water by upwards leakage of shale gas components, such as methane (Kerr, 2011; Krupnick et al., 2011).
- Both of these (Lustgarten, 2009)

(Wood et al., 2011) state that the potential for groundwater contamination is a key risk associated with shale gas extraction. This could occur if there is a catastrophic failure or loss of integrity of the wellbore, or if contaminants can travel from the target fracture through subsurface pathways. This review draws on a number of other articles, including (Energy and Climate Change Select Committee, 2011; McNutt, 2011; Ridley, 2011; Zoback et al., 2010) to set out the potential concerns in the following chapters.

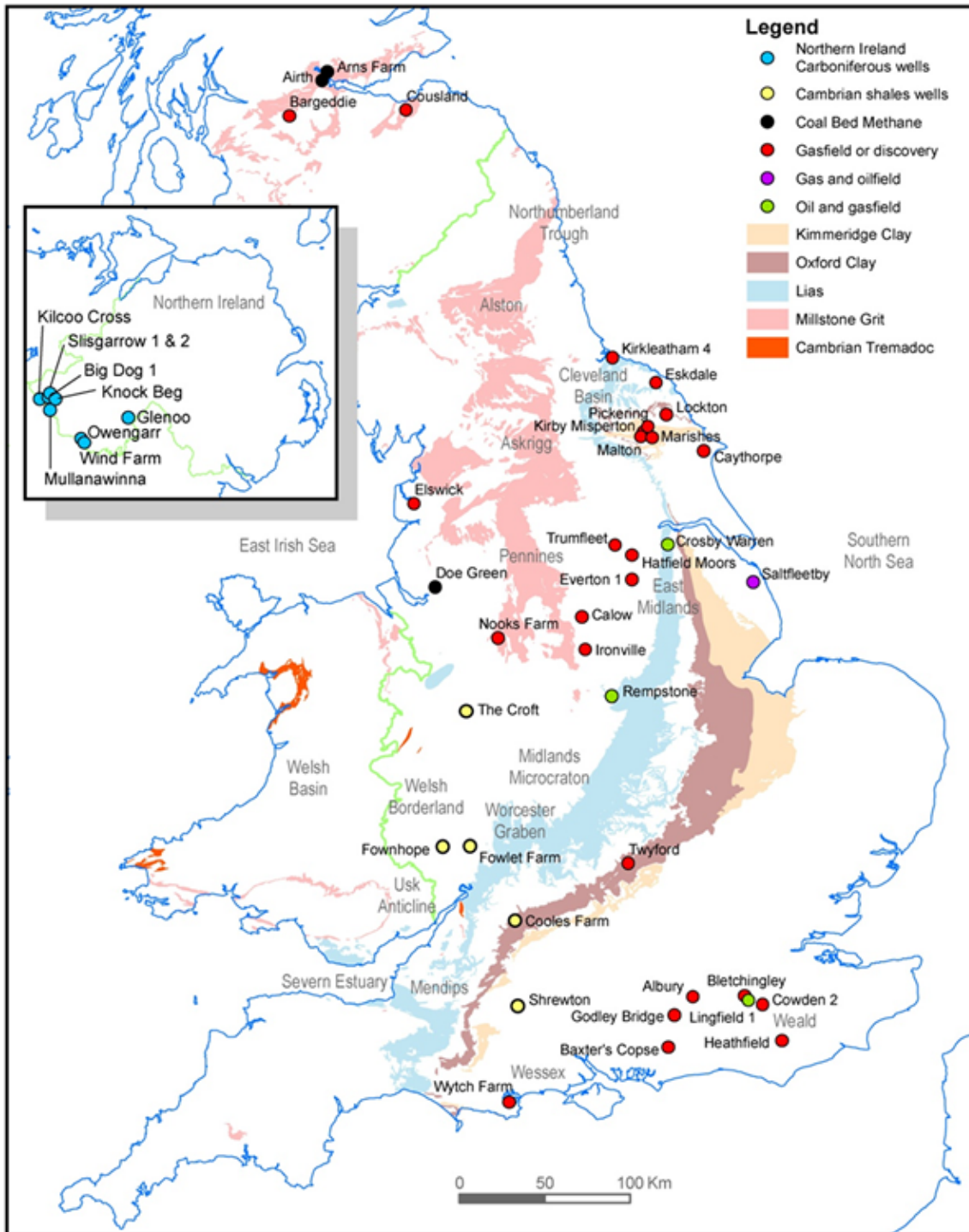


Figure 1.5 Outcrop of main black shale formations in UK and selected oil and gas wells and gas fields.

2 Water resources issues

The sheer volume of water consumed during hydraulic fracturing could make unconventional gas production costly and unsustainable in many areas of the world that are water-constrained (Flavin and Kitasei, 2010). The drilling and completion of wells require large quantities of water (Gregory et al., 2011). Drilling of the vertical and horizontal components of a well may require 400–4000 m³ of water for drilling fluids to maintain downhole hydrostatic pressure, cool the drill head, and remove drill cuttings. Then, 7000–18,000 m³ of water are needed for hydraulic fracturing of each well. These large volumes of water are typically obtained from nearby surface waters or pumped from a municipal source. Such water is not generally returned to surface or groundwater.

Wood et al. (2011) give an estimate for the UK of the range of water resources potentially required per year to deliver sustained annual production (over a period of 20 years) equivalent to 10% of the UK's annual consumption (annual gas consumption in the UK in 2008 was around 90bcm). This was for six well pads drilled vertically to 2000 m and laterally to 1200 m and for 50% of these to require refracturing once (Table 2.1).

Potential impacts, where no controls are in place, are listed in New York State (2011) as modifications to groundwater levels, surface water levels and stream flow. Operators need this water when drilling activity is occurring, requiring that the water be procured over a relatively short period of time. Water withdrawals during periods of low stream flow could affect fish and other aquatic life, fishing and other recreational activities, municipal water supplies, and other industries such as power plants (Ground Water Protection Council and ALL Consulting, 2009). This can impact ecology, for example due to unsuitable water temperatures and dissolved oxygen concentrations during periods of low flow (New York State, 2011). In regions where local, natural water sources are scarce or dedicated to other uses, the limited availability of water may be a significant impediment to gas resource development (Ground Water Protection Council and ALL Consulting, 2009).

Table 2.1 Summary of water resources required to meet 10% of UK annual requirement for gas (Wood et al., 2011)

	Activity	Volume (m ³)	
		Min	Max
Initial fracturing	Water volume	54,000	174,000
	Fracturing chemicals volume (@2%)	1,080	3,480
	Flowback water	7,920	137,280
	Flowback water waste content (@2%)	158	2,746
Refracturing	Water volume	27,000	87,000
	Fracturing chemicals volume (@2%)	540	1,740
	Flowback water	3,960	68,640
	Flowback water waste content (@2%)	79	1,373

3 Contamination issues

3.1 SOURCES

3.1.1 Constituents of shale gas

Shale-gas systems essentially are continuous-type biogenic (predominant), thermogenic, or combined biogenic-thermogenic gas accumulations characterized by widespread gas saturation, subtle trapping mechanisms, seals of variable lithology, and relatively short hydrocarbon migration distances. Shale gas may be stored as free gas in natural fractures and intergranular porosity, as gas sorbed onto kerogen and clay-particle surfaces, or as gas dissolved in kerogen and bitumen (Jenkins and Boyer, 2008). Shale gas has calorific values at the high end of the range for natural gas (c.1200 btu)(Selley, 2005).

Natural gas is considered 'dry' when it is almost pure methane; when other hydrocarbons are present, the natural gas is 'wet.' (Natural Gas Supply Association, 2010) In general thermogenic gas has a high methane content with low but significant concentrations of higher hydrocarbons such as ethane (C₂) and propane (C₃), with C₁/(C₂+C₃) <100, and enriched ¹³C with δ¹³C methane in the range -110 to -55‰. In contrast biogenic gas has C₁/(C₂+C₃) between 1000 to 10,000 and δ¹³C methane in the range -55 to -20‰ (Révész et al., 2010). Typical values for natural gas are shown in Table 3.1.

Table 3.1 Typical composition of gas (from Natural Gas Supply Association, 2010)

Name	Formula	Typical content (%)
Methane	CH ₄	70–90
Ethane	C ₂ H ₆	0–20
Propane	C ₃ H ₈	
Butane	C ₄ H ₁₀	
Carbon dioxide	CO ₂	0–8
Oxygen	O ₂	0–0.2
Nitrogen	N ₂	0–5
Hydrogen sulphide	H ₂ S	0–5
Rare gases	Ar, He, Ne, Xe	Trace

For the Fort Worth Shale methane varies in concentration from 75% in the northwest to 96% in the southeast part of the study area (Rodriguez and Philp, 2010). A general increase in the methane concentration can be observed from west to east in the study area, which has been interpreted as the consequence of an increase in maturity in the same direction. It was all assumed to be derived from kerogen cracking and secondary cracking of non-migrated hydrocarbons.

The molecular composition of the Antrim Shale, USA varies from almost pure methane to 5% by volume of ethane and higher hydrocarbons, nitrogen and carbon dioxide (Martini, A M et al., 1996). Gas at margins of the basin was considered to have a microbial origin on the basis of high methane content and shallow depth of production. The δ¹³C isotopic signature of gas and co-produced water suggested microbial methanogenesis. There was also correlation of δD of methane and formation water. Along the basin margins systematic enrichment of C₂ and C₃ with depletion of concentration suggesting oxidation of higher alkanes (Martini, Anna M. et al., 2003). These isotopic signatures allow potential contamination by shale gas to be identified.

3.1.2 Fracking chemicals

The following details are summarised from Gregory et al. (2011) and set out in Table 3.2. After water, the largest compound of a fracture fluid utilized to treat a shale gas wells is proppant. Proppant is a granular material, usually sand, which is mixed with the fracture fluids to hold or prop open the created fractures that allow gas to flow to the well. Other commonly used proppants include resin- coated sand, intermediate strength proppant ceramics, and high strength proppants such as sintered bauxite and zirconium oxide. Resin coated sands are utilized regularly in the shale gas plays during the final stages of a fracture. Resin coating may be applied to improve proppant strength or may be design to react and act as a glue to hold some of the coated grains together.

Table 3.2 Composition and purposes of typical constituents of hydraulic fracturing fluid (after Gregory, 2011 and Ground Water Protection Council and ALL Consulting, 2009)

Constituent	Composition (% by volume)	Example	Purpose
Water and sand	99.50	Sand suspension	“Proppant” sand grains hold microfractures open
Acid	0.123	Hydrochloric or muriatic acid	Dissolves minerals and initiates cracks in the rock
Friction reducer	0.088	Polyacrylamide or mineral oil	Minimizes friction between the fluid and the pipe
Surfactant	0.085	Isopropanol	Increases the viscosity of the fracture fluid
Salt	0.06	Potassium chloride	Creates a brine carrier fluid
Scale inhibitor	0.043	Ethylene glycol	Prevents scale deposits in pipes
pH-adjusting agent	0.011	Sodium or potassium carbonate	Maintains effectiveness of chemical additives
Iron control	0.004	Citric acid	Prevents precipitation of metal oxides
Corrosion inhibitor	0.002	n,n-dimethyl formamide	Prevents pipe corrosion
Biocide	0.001	Glutaraldehyde	Minimizes growth of bacteria that produce corrosive and toxic by-products
Breaker	0.01	Ammonium persulphate	Allows a delayed breakdown of gel polymer chains
Crosslinker	0.007	Borate salts	Maintains fluid viscosity as temperature increases
Gelling agent	0.056	Guar gum or hydroxyethyl cellulose	Thickens water to suspend the sand
Oxygen scavenger	-	Ammonium bisulphite	Removes oxygen from the water to prevent corrosion

The viscosity of fresh water tends to be low, which limits waters ability to transport the proppant necessary for a successful fracture stimulation treatment. As a result, some hydraulic fracturing fluids have a gel additive to increase the viscosity of fracture fluids, typically, either a linear or a cross-linked gel. Gellant selection is based on reservoir formation characteristics, such as thickness, porosity, permeability, temperature, and pressure. As temperatures increase, these gels tend to thin dramatically. In order to prevent the loss of viscosity, polymer concentration can be

increased (polymer loading) or instead, cross-linking agents can be added to increase the molecular weight, thus increasing the viscosity of the solution.

In addition to water and proppant, many other additives are essential to successful shale gas reservoir fracture stimulation. Acid is utilized in the beginning of the fracture process to clean up cement that is lodged in the perforations and provide an accessible path to the formation once fracturing fluid is pumped. Hydrochloric acid is most commonly used at a concentration of 15% HCl although it can effectively be utilized in concentrations ranging from 3% to 28%. Acids are typically diluted to desired concentrations prior to transporting to the job location. Once it is added to the fluids, it is further diluted by a factor of 1,000 or more prior to subsurface injection. In stimulations that utilize an acid breakdown, a corrosion inhibitor is used to hinder the corrosion of steel tubing, well casing, tools and tanks. The addition of 0.1% to 2% of a corrosion inhibitor can decrease corrosion by up to 95%. Concentrations of corrosion inhibitor depend on downhole temperatures and casing and tubing types. At temperatures exceeding 250 degrees Fahrenheit, higher concentrations of corrosion inhibitor, a booster, or an intensifier may also be necessary. A typical corrosion inhibitor utilized in shale gas plays is n,n-dimethyl formamide.

Biocides are additives that are used to minimize the danger of bacterial corrosion in the wellbore. Fracture fluids typically contain gels that are organic, which provides an ideal medium for bacterial growth, reducing viscosity and the ability of the fluid to effectively carry proppant. Biocides, such as glutaraldehyde are diluted in the fluid in a mannerism similar to the addition of the corrosion inhibitor. In addition to glutaraldehyde, biocides can also contain bleach, DAZOMET, or 2,2-dibromo3-nitrilopropionamide. When a formation contains clay, permeability can be significantly reduced when exposed to water that is less saline than the formation water. As a result, treatment with solutions containing 1% to 3% salt is generally utilized as a base liquid when clay swelling is probable. Potassium chloride (KCl) is the most common chemical utilized as a clay stabilizer due to its ability to stabilize clay against the invasion of water to prevent swelling.

However, in wells that have lower temperatures, such as the shale gas wells in the Barnett and Fayetteville plays, a breaker is added to the fluid in later stages of the process to break down the viscosity of the gelling agent to aid in releasing the proppant and enhance the volume of flowback water received after the completion. The most common type of breaker is peroxydisulphate. Breakers are typically added as the gel is being pumped because if given enough time, it could reduce the viscosity prior to pumping.

3.1.3 Naturally occurring radioactive material

Naturally occurring radioactive material can be brought to the surface in the natural gas production process. When such material is associated with oil and natural gas production, it begins as small amounts of uranium and thorium within the rock. These elements, along with some of their decay elements, notably Ra²²⁶ and Ra²²⁸, can be brought to the surface in drill cuttings and produced water. Radon²²², a gaseous decay element of radium, can come to the surface along with shale gas (Ground Water Protection Council and ALL Consulting, 2009). The principal concerns are with accumulation in field equipment or in sludge or sediment within settling tanks.

3.2 ROUTES TO GROUNDWATER

3.2.1 Fracking process

A frequently expressed concern about shale gas development is that subsurface hydraulic fracturing operations in deep shale formations might create fractures that extend well beyond the target formation to water aquifers, allowing methane, contaminants naturally occurring in formation water, and fracturing fluids to migrate from the target formation into drinking water supplies (Zoback et al., 2010). Because the direct contamination of underground sources of

drinking water from fractures created by hydraulic fracturing would require hydrofractures to propagate several thousand feet beyond the upward boundary of the target formation through many layers of rock, such contamination is highly unlikely to occur in deep shale formations during well-designed fracture jobs. A report for New York State (2011) concludes that fracking is unlikely to create a pathway beyond the fractured zone and the post fracking reversal of pressure means that fluids migrate back to the well.

The successful injection of hydraulic fracturing fluid is intended to result in gas production without the contamination of groundwater. This depends on the integrity of the well and the correct fluid design (Arthur et al., 2009).

Zoback et al. (2010) state that seismic monitoring is an essential tool for assuring that hydraulic fracturing is inducing microseismic activity only within the shale gas reservoir. Yet only about three percent of the ~75,000 hydraulic fracturing stages conducted in the United States in 2009 were seismically monitored. These authors suggested that public confidence in the safety of hydraulic fracturing would be greatly improved by more frequent microseismic monitoring and public dissemination of the results.

Another subsurface risk that has received attention recently is the possibility that drilling and hydraulically fracturing shale gas wells might cause low-magnitude earthquakes. While the hydraulic fracturing process does create a large number of microseismic events, or micro-earthquakes, the magnitudes of these are generally too small to be detected at the surface (Zoback et al., 2010).

Underground fluid injection is an integral part not only of hydraulic fracturing, but of waste water disposal in injection wells, some geothermal energy projects, and carbon dioxide sequestration. The seismic monitoring of hydraulic fracture jobs discussed earlier is critical to improving understanding of how underground injection might spark unexpectedly high magnitude seismic activity.

3.2.2 Accidental releases during preparation of fracturing fluids

New York State (2011) list potentially polluting activities as fuelling and tank refilling, bulk chemical or fluid storage, equipment cleaning, vehicle maintenance, pipe work, cement mixing areas and piping. On-site spills or leaks could potentially occur during transport to site and mixing and preparation. (Zoback et al., 2010) report that up to 200 additives could be used in fracturing fluids. Chemicals to be used in fracturing fluids are commonly transported by road and are generally stored at drilling sites in tanks before they are mixed with water in preparation for a fracturing job. These could therefore be released by pipe work or regulator failures or by operator error (Wood et al., 2011). These fluids have the potential to contaminate surface water and groundwater in the same way as any other surface activity.

3.2.3 Fluid leak-offs, blowouts and casing failures

All natural gas wells are subject to accidents such as blowouts, improper well construction and abandonment and associated contamination. Any structure that penetrates water aquifers, such as a well, has the potential to contaminate these water sources (Grubert and Kitasei, 2010).

The loss of fracturing fluid through the artificially created fractures to other areas within the shale gas formation is termed fluid leak off. This can constitute 70% of the injected volume if not controlled properly which could result in fluid migrating into drinking water aquifers (Energy and Climate Change Select Committee, 2011).

Failure of the cement or casing surrounding the wellbore poses a risk to water supplies. If the annulus is improperly sealed, natural gas, fracturing fluids, and formation water containing high concentrations of dissolved solids may be communicated directly along the outside of the wellbore among the target formation, drinking water aquifers, and layers of rock in between.

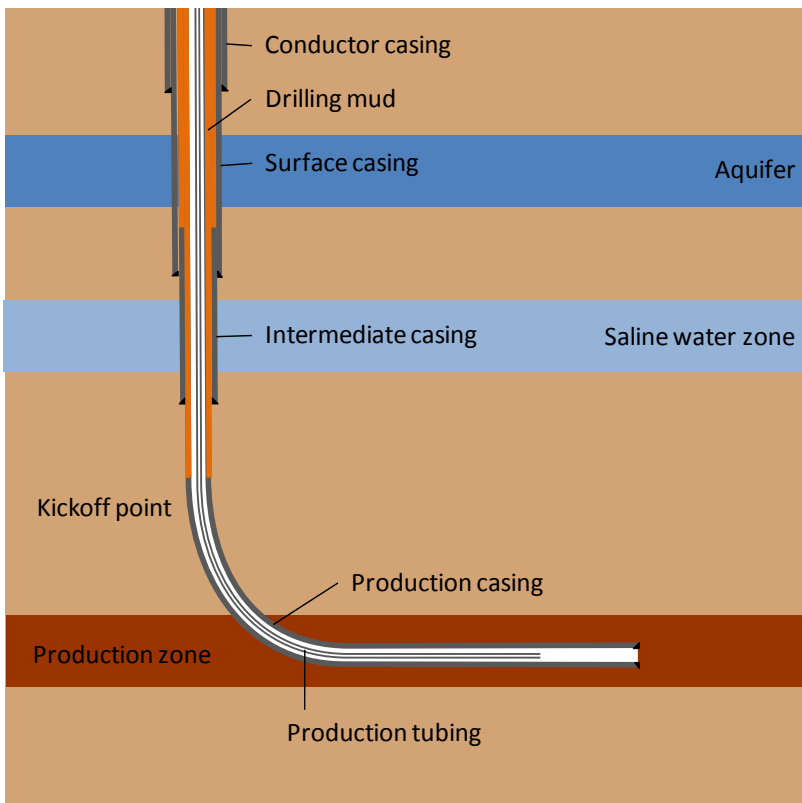


Figure 3.1 Schematic of casing and grouting to protect groundwater resources (from (Ground Water Protection Council and ALL Consulting, 2009))

As a further protection of the fresh water zones, air-rotary drilling is often used when drilling through this portion of the wellbore interval to ensure that no drilling mud comes in contact with the fresh water zone. Intermediate casings, when installed, are used to isolate non freshwater-bearing zones from the producing wellbore. Intermediate casing may be necessary because of a naturally over-pressured zone or because of a saltwater zone located at depth. The borehole area below an intermediate casing may be uncemented until just above the kickoff point for the horizontal leg. This area of wellbore is typically filled with drilling muds.

Analysis of the redundant protections provided by casings and cements was presented in a series of reports and papers prepared for the American Petroleum Institute (API) in the 1980s. These investigations evaluated the level of corrosion that occurred in Class II injection wells. Class II injection wells are used for the routine injection of water associated with oil and gas production. The research resulted in the development of a method of calculating the probability (or risk) that fluids injected into injection wells could result in an impact to a drinking water source.

Detailed analysis was performed for those basins in which there was a possibility of casing corrosion (Michie & Associates, 1988). Risk probability analysis provided an upper bound for the probability of the fracturing fluids reaching an underground source of drinking water. Based on the values calculated, a modern horizontal well completion in which 100% of the USDWs are protected by properly installed surface casings (and for geologic basins with a reasonable likelihood of corrosion), the probability that fluids injected at depth could impact a USDW would be between 2×10^{-5} (one well in 200,000) and 2×10^{-8} (one well in 200,000,000) if these wells were operated as injection wells. Other studies in the Williston basin found that the upper bound probability of injection water escaping the wellbore and reaching an underground source of drinking water is seven changes in one million well-years where surface casings cover the drinking water aquifers (Michie and Koch, 1991).

3.2.4 Flowback and produced water

Most of the concerns of water transport and disposal arise from flowback water which is produced by the fracturing process or produced water which comes from the formation during gas production, or the partial recovery of the fluids that are utilized to fracture stimulation a well.

Flowback of the fracturing fluid occurs over a few days to a few weeks following hydraulic fracturing, depending on the geology and geomechanics of the formation. The highest rate of flowback occurs on the first day, and the rate diminishes over time; the typical initial rate may be as high as 1000 m³/d (Arthur et al., 2008). The majority of fracturing fluid is recovered in a matter of several hours to a couple of weeks. In various basins and shale gas plays, the volume of produced water may account for less than 30% to more than 70% of the original fracture fluid volume. In some cases, flow back of fracturing fluid in produced water can continue for several months after gas production has begun (Ground Water Protection Council and ALL Consulting, 2009).

The dissolved constituents are naturally occurring compounds and may vary from one area to the next or even by area within the same shale. Initial produced water can vary from fresh (<5,000 mg/L TDS to varying degrees of saline (5,000 mg/L to 100,000 mg/L TDS or higher). Typical ranges of composition are shown in Table 3.3. The composition of the flowback water changes as a function of the time the water flowing out of the shale formation. A comprehensive list of constituents including priority pollutants is provided in Appendix 1 of this report.

There is growing public concern about management of this water because of the potential for human health and environmental impacts associated with an accidental release of flowback water into the environment (Kargbo et al. 2010). Past experience with produced and flowback waters is used to guide developers towards treatment and management options in regions of new production (Kargbo et al. 2010). Flowback water management options for some shale plays, such as the Marcellus, are confounded by high concentrations of total dissolved solids in the flowback water, geography, geology, and a lack of physical infrastructure (Arthur et al. 2008; Kargbo et al. 2010).

Table 3.3 Range of constituents in flowback water from development in the Marcellus Shale, USA (after Gregory et al, 2011)

Constituent	Low(mg/L)	Medium (mg/L)	High (mg/L)
Total dissolved solids	66,000	150,000	261,000
Total suspended solids	27	380	3200
Hardness (as CaCO ₃)	9100	29,000	55,000
Alkalinity (as CaCO ₃)	200	200	1100
Chloride	32,000	76,000	148,00
Sulphate	-	7	500
Sodium	18,000	33,000	44,000
Calcium	3000	9800	31,000
Strontium	1400	2100	6800
Barium	2300	3300	4700
Bromide	720	1200	1600
Oil and grease	10	18	260

3.2.5 Retention pits

In rural areas, storage pits may be used to hold fresh water for drilling and hydraulic fracturing (Ground Water Protection Council and ALL Consulting, 2009). They are typically excavated containment ponds that, based on the local conditions and regulatory requirements, may be lined. Water storage pits are becoming an important tool in the shale gas industry because the drilling and hydraulic fracturing of these wells often requires significant volumes of water as the base fluid for both purposes. Pits can also be used to store additional make-up water for drilling fluids or to store water used in the hydraulic fracturing of wells.

In an urban setting, due to space limitations, steel storage tanks may be used. Tanks can also be used in a closed-loop drilling system. Closed-loop drilling allows for the re-use of drilling fluids and the use of lesser amounts of drilling fluids. Closed-loop drilling systems have also been used with water-based fluids in environmentally sensitive environments in combination with air-rotary drilling techniques. While closed-loop drilling has been used to address specific situations, the practice is not necessary for every well drilled. As discussed in the previous section, drilling is a regulated practice managed at the state level, and while state oil and gas agencies have the ability to require operators to vary standard practices, the agencies typically do so only when it is necessary to protect the gas resources and the environment.

3.2.6 Disposal of flowback liquid

3.2.6.1 INJECTION UNDERGROUND THROUGH AN ONSITE OR OFFSITE WELL

Most produced water from oil and gas production in the United States is disposed of through deep underground injection. However, the availability of adequate deep-well disposal capacity can be an important constraining factor for shale gas development. As a result, other solutions for flowback water management are necessary (Gregory et al., 2011).

3.2.6.2 DISCHARGE TO NEARBY SURFACE WATER

This option is generally infeasible due to the quality of the water to be disposed.

3.2.6.3 TRANSPORT TO TREATMENT WORKS EITHER MUNICIPAL OR INDUSTRIAL

Although discharge and dilution of flowback water into publicly owned municipal wastewater treatment plants (WWTWs) has been utilized in the USA, (Gregory et al., 2011) state that this is not an adequate or sustainable approach for managing flowback water. The amount of high-TDS flowback water that can be accepted by WWTWs is usually limited by regulation. In general, the volume of flowback water that can be sent to WWTWs is small compared to the volume of flowback water generated during rapid well drilling and well development. New York State (2011) state that purpose-built private treatment systems are more likely to be effective in treating flowback water than municipal WWTWs.

Even with favourable energy prices, the treatment of flowback water using RO is considered to be economically infeasible for waters containing more than 40,000 mg/L TDS. For high-TDS waters, vibratory shear-enhanced processing (VSEP) has been applied to membrane technologies. However, the salt concentrations in offshore produced waters are far lower than those expected during shale gas extraction.

The high concentrations of TDS in flowback water may limit the use of membrane technology, but such water is well suited to treatment by distillation and crystallization. Distillation and crystallization are mature technologies that rely on evaporating the wastewater to separate the water from its dissolved constituents. The vapour stream is passed through a heat exchanger to condense the gas and produce purified water. Distillation removes up to 99.5% of dissolved solids and has been estimated to reduce treatment and disposal costs by as much as 75% for produced water from shale oil development. However, as with RO, distillation is an energy-intensive process. Thermal distillation may treat flowback water containing up to, and in some

cases even exceeding, 125,000 mg/L of TDS, but even the most modern technology is limited to low flow rates (300 m³/d), necessitating the construction of large storage impoundments. Crystallization is a feasible approach for treating flowback water with TDS concentrations as high as 300,000 mg/L, but it has high energy requirements and large capital costs.

Several other technologies have been or are being developed for treating flowback water, but each has its limitations. Ion exchange and capacitive deionization are limited to the treatment of low-TDS water; freeze–thaw evaporation is restricted to cold climates; evaporation ponds are restricted to arid climates; and artificial wetlands and agricultural reuse are greatly limited by the alkalinity tolerance of plant and animal life.

3.2.6.4 REUSE

One of the most promising technologies for management of flowback water is its reuse in subsequent hydraulic fracturing operations. Flowback water is impounded at the surface and reused either directly or following dilution or pre-treatment. Reuse is particularly attractive in regions where deep-well disposal options are limited or where the availability of make-up water for hydraulic fracturing is limited. The reuse of flowback water has the benefit of minimizing the volume of such water that must be treated or disposed of and greatly reduces environmental risks while enhancing the economics of shale gas extraction. Potentially limiting factors for reuse are the chemical stability of the viscosity modifiers and other constituents of hydraulic fracture water in the brine solution and the potential for precipitation of divalent cations in the wellbore.

The effectiveness of friction reducers may be decreased at high TDS concentrations. The development of additives that retain their effectiveness in brine solutions are likely to expand the opportunity for reuse of flowback water for subsequent hydraulic fracturing.

However, the major problem with use of flowback water for makeup of hydrofracking water is the very high concentration of scale forming constituents including barium, calcium, iron, magnesium, manganese, and strontium (Ba, Ca, Fe, Mg, Mn, and Sr). The divalent cations in the flowback water are solubilised from formation minerals and can form stable carbonate and sulphate precipitates in the wellbore if the flowback water is reinjected. This may potentially reduce gas production from the well. In particular, barium and strontium form very low-solubility solids with sulphate, while high calcium concentrations may lead to calcite formation. These constituents readily form precipitates which rapidly block the fractures in gas bearing formations required for economic gas production. Reusable flowback water should have a maximum total hardness of 2,500 mg/L measured as CaCO₃ (Kargbo et al., 2010). Depending on the quality of the flowback water, pre-treatment to reduce the divalent cation concentration by precipitation may be necessary.

4 Evidence of groundwater contamination

There is evidence of surface water contamination from shale gas production. A number of incidents are documented in New York State (2011) related to fracturing fluid releases and uncontrolled release of flowback water. Fracturing fluid releases occurred during mixing and pumping of fluid and resulted in surface water pollution by mixed fluid rather than the concentrated components. Flowback water was released together with gas and brine during post fracturing cleanout of a borehole due to inadequate blowback prevention equipment.

There are very few scientific studies that have assessed the impact of shale gas extraction on groundwater. The examples below all relate to the detection of shale gas constituents in groundwater.

In 2007, a well that had been drilled almost 1200 m into a tight sand formation in Bainbridge, Ohio was not properly sealed with cement, allowing gas from a shale layer above the target tight sand formation to travel through the annulus into an underground source of drinking water. The methane eventually built up until an explosion in a resident’s basement alerted state officials to the problem (Ohio Dept of Natural Resources, 2008).

In aquifers overlying the Marcellus and Utica shale formations of north-eastern Pennsylvania and upstate New York, (Osborn et al., 2011) document systematic evidence for methane contamination of drinking water associated with shale gas extraction. In active gas-extraction areas (one or more gas wells within 1 km), average and maximum methane concentrations in drinking-water wells increased with proximity to the nearest gas well and were 19.2 and 64 mg CH₄ L⁻¹ (n=26), a potential explosion hazard; in contrast, dissolved methane samples in neighbouring non-extraction sites (no gas wells within 1 km) within similar geologic formations and hydrogeological regimes averaged only 1.1 mgL⁻¹ (P < 0.05; n=34) (Figure 4.1).

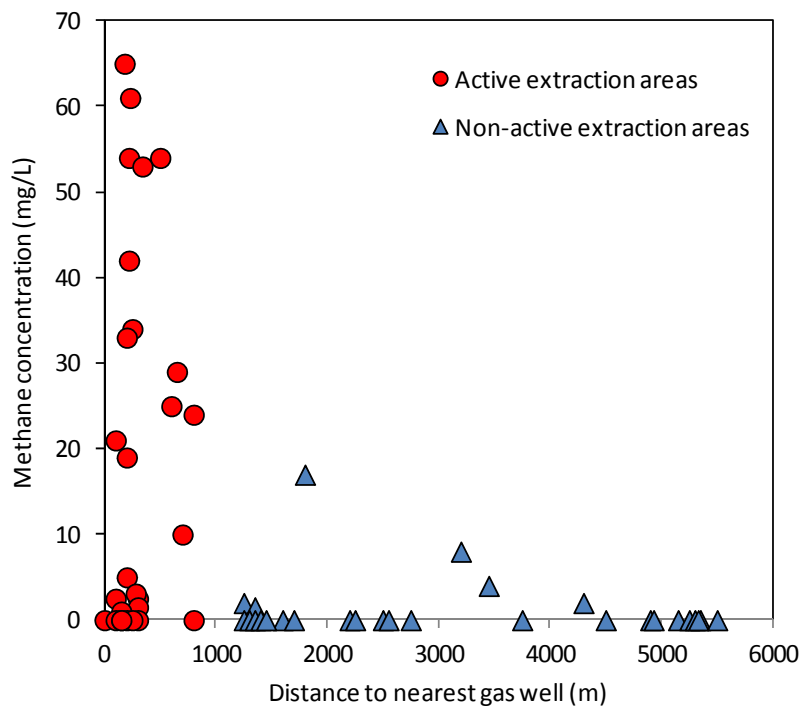


Figure 4.1 Methane concentrations as function of distance to nearest gas well (from (Osborn et al., 2011))

Average $\delta^{13}\text{C-CH}_4$ values of dissolved methane in shallow groundwater were significantly less negative for active than for non-active sites (-37.7‰ and -54.1‰ , respectively; $P < 0.0001$). These $\delta^{13}\text{C-CH}_4$ data, coupled with the ratios of methane-to-higher-chain hydrocarbons, and $\delta^2\text{H-CH}_4$ values, are consistent with deeper thermogenic methane sources such as the Marcellus and Utica shales at the active sites and matched gas geochemistry from gas wells nearby. In contrast, lower-concentration samples from shallow groundwater at non-active sites had isotopic signatures reflecting a more biogenic or mixed biogenic/thermogenic methane source. They found no evidence for contamination of drinking-water samples with deep saline brines or fracturing fluids.

Révész et al. (2010) investigated the origin of the combustible gases in groundwater from glacial-outwash and fractured-bedrock aquifers in northern Tioga County, Pennsylvania. Thermogenic methane (CH_4) and ethane (C_2H_6) and microbial CH_4 were found. Microbial CH_4 is from natural in situ processes in the shale bedrock and occurs chiefly in the bedrock aquifer. The $\delta^{13}\text{C}$ values of CH_4 and C_2H_6 for the majority of thermogenic gases from water wells either matched or were between values for the samples of non-native storage-field gas from injection wells and the samples of gas from storage-field observation wells. Traces of C_2H_6 with microbial CH_4 and a range of C and H isotopic compositions of CH_4 indicate gases of different origins are mixing in sub-surface pathways; gas mixtures are present in groundwater. Pathways for gas migration and a specific source of the gases were not identified. Processes responsible for the presence of microbial gases in groundwater could be elucidated with further geochemical study.

5 Standards and regulation

5.1 UK

Broderick et al. (2011) reviewed the key regulatory instruments in place in the UK and the EU in the context of control of risks and impacts of shale gas exploration and commercial development.

Control and oversight of chemicals used in fracturing fluid is in theory provided by the European REACH Regulations (HSE, 2008), but as yet none of the substances examined by the European Chemicals and Health Agency has yet been registered for use in fracturing fluids.

Environmental impacts come under the scope of the Environmental Impact Assessment Directive (EC, 2009), but the volume of gas from individual production units are lower than the minimum to require their classification as Annex I and the assessment of Annex II projects is not consistently applied across the EU. No EIAs have been undertaken at existing UK sites as these are being below the minimum area.

Drilling standards have been recently summarised in Pereira (2011). Unconventional resources were not a consideration when the current regulations were made in the 1990s; for this reason, no specific mention of horizontal directional drilling and hydraulic fracturing is made in the regulations used in shale gas production, the Borehole Sites and Operations Regulations 1995 and the Well aspects of the Offshore Installations and Wells (Design and Construction, etc.) Regulations 1996.

For shale gas production, the technologies of hydraulic fracturing and horizontal directional drilling are the same as those of conventional drilling and have been in use for a long time but there are a lack of standards for these processes. There are British Standards covering hydraulic fracturing proppants and hydraulic fluid power, however, there are none covering chemicals used or the fracking procedure itself (BSI, 2009). A standard on directional drilling is under development (BSI, under development). Pereira (2011) therefore states that the unique element of hydraulic fracturing to unconventional gas exploration introduces dangers from pressurised water as well as chemical and water spillages and that it is clear that British and ISO standards are lacking in this area. They recommend that “standards are needed in the UK and

internationally to ensure the consistency of safety measures and to guarantee that damaging or dangerous practices such as those that have been recorded in the UK do not occur within the UK.

In England and Wales, the Environment Agency is responsible for managing the environmental risks of gas drilling onshore and up to one nautical mile offshore, which directly relate to potential pollution of water and large-scale refinement combustion. They would require information about the chemicals used in the fluid if the site is assessed as posing a risk to groundwater could require the operator to apply for a permit. All risks, including seismic activity are included. Of the 5 site permit and two are as yet unassessed. Measures that are currently mandatory for all fracking sites are an impermeable membrane to prevent spills entering the soil, and bunding to contain leakages. Currently flowback water is monitored for pollutants and radioactive material, but would not normally be tested from the site where a permit is not required.

US

5.2 USA

Where shale gas exploitation is established regulations are in place to minimise environmental impact. For example, regulations to minimise the risk of water impact are set out by New York State (2011) as:

- Any proposed high-volume hydraulic fracturing where the top of the target fracture zone is shallower than 2,000 feet (~600 m) along a part of the proposed length of the wellbore;
- Any proposed high-volume hydraulic fracturing where the top of the target fracture zone at any point along the entire proposed length of the wellbore is less than 1,000 feet (~300 m) below the base of a known fresh water supply;
- Any proposed well pad within the boundaries of a principal aquifer, or outside but within 500 feet (~150 m) of the boundaries of a principal aquifer;
- Any proposed well pad within 150 feet (~45 m) of a perennial or intermittent stream, storm drain, lake or pond;
- A proposed surface water withdrawal that is found not to be consistent with the Department's preferred passby flow methodology;
- Any proposed well location determined by the New York City Department of Environmental Protection to be within 1,000 feet (~300 m) of its subsurface water supply infrastructure.

6 Conclusions

6.1 SUMMARY

- The UK may possess considerable reserves of shale gas. Significant areas include the carboniferous strata of the Widmerpool Gulf, near Nottingham, and the Elsewick field near Blackpool. Work to extract shale gas has begun near Blackpool.
- Shale gas is predominantly methane of thermogenic origin with low percentages of C₂ and C₃ hydrocarbons. Its ¹³C isotopic signature allows it to be distinguished from shallow biogenic methane in the subsurface
- Extraction involved drilling of deep horizontal wells and enhancing the natural permeability of the shale by hydraulic fracturing.
- Groundwater may be potentially contaminated by extraction of shale gas both from the constituents of shale gas itself, from the formulation and deep injection of water containing a cocktail of additives used for hydraulic fracturing and from flowback water which may have a high content of saline formation water.

- Fracking chemicals include hydrochloric acid, polyacrylamide, mineral oil, isopropanol, potassium chloride and ethylene glycol and low concentrations of pH buffers, corrosion inhibitors, biocides and gelling agents.
- A wide range of pollutants, including priority substances has been detected in flowback water
- The large volumes of water required may also put pressure on groundwater resources with impacts on other uses and groundwater dependent ecosystems. Reuse of flowback water involves treatment to remove high TDS.
- There are examples of surface water contamination from releases of fracturing water or flowback water. Documented instances of groundwater contamination from the U.S. are all related to the leakage of methane into groundwater.

6.2 UNKNOWNNS

- For UK whether fields likely to be exploited for shale gas are overlain by significant aquifers.
- Vulnerability of groundwater to surface pollution from operations and flowback water. For aquifers at outcrop this can be informed by existing vulnerability mapping and other information
- Vulnerability of groundwater to pollution from fracking operations and shale gas. Relative depths of groundwater and shale gas reservoirs and the nature of the intervening strata. As an example a schematic for the U.S. shale gas plays is shown in Figure 6.1.

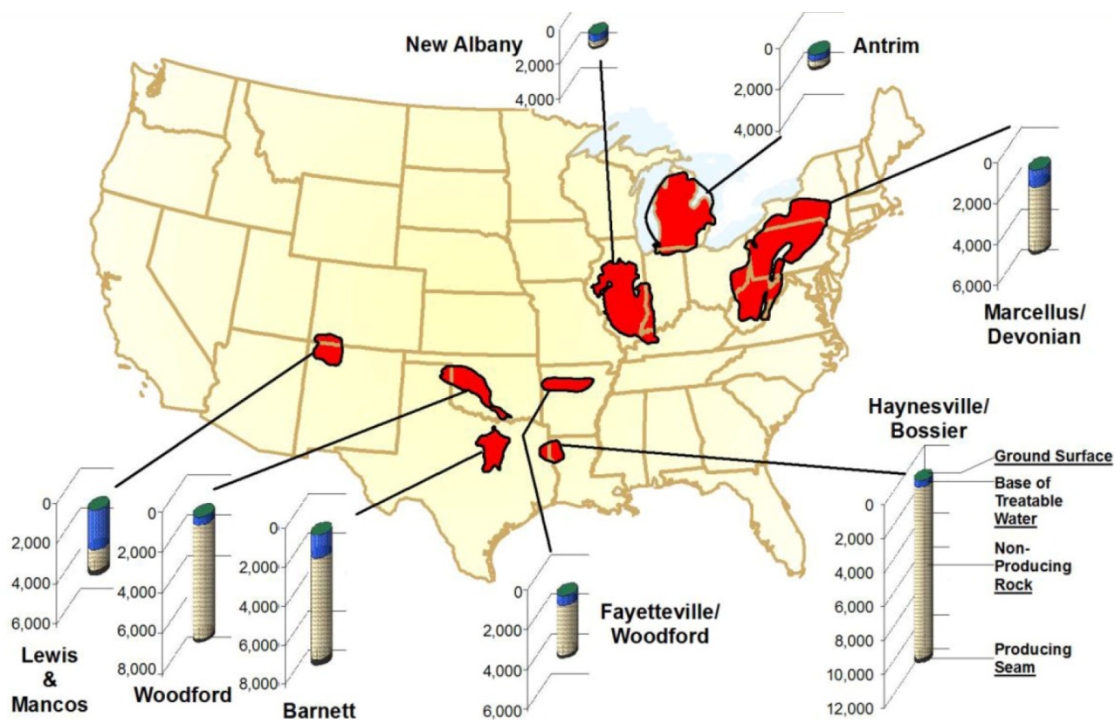


Figure 6.1 Comparative depths of shale gas formations and groundwater for the U.S. (Ground Water Protection Council and ALL Consulting, 2009)

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Appendix 1 Chemical constituents of fracturing fluid and flowback water

Table A1 Chemical constituents of products used in fracturing fluid (Wood et al 2010 taken from (New York State, 2009))

Substance	Controlled Substance*	Substance	Controlled Substance*
1,2 Benzisothiazolin-2- one / 1,2-benzisothiazolin-3-one		Hydroxylamine hydrochloride	
1,2,4 Trimethylbenzene	HS	Isopropylbenzene (cumene)	
1,4 Dioxane		Light aromatic solvent naphtha	
2-Bromo-2-nitro-1,3- propanediol		Methanol	
2-Butoxy ethanol		Mineral spirits / Stoddard Solvent	
2-Propyn-1-ol		Monoethanolamine	
3,5,7-Triaza-1- azoniatricyclo [3.3.1.1 ^{3,7}]decane, 1-(3-chloro-2-propenyl)-		Naphtha (petroleum), hydrotreated heavy	HS
Acetic anhydride		Naphthalene	HS/PS
Acrylamide		Naphthalene bis(1- methylethyl)	
Ammonia	NHP	Petroleum base oil	
Ammonium hydrogendifluoride		Petroleum naphtha	
Ammonium persulfate		Potassium hydroxide	
Aqueous ammonia	NHP	Propylene glycol monomethyl ether	
Benzene	HS/PS	Sodium bisulphate	
Boric acid		Sodium chloroacetate	
Butan-1-ol		Sodium hydroxide	
Chlorine dioxide		Sodium hypochlorite	NHP
Copper (II) sulphate	NHP	Sodium tetraborate decahydrate	NHP
Diethylene glycol		Sulfamic acid	
Ethyl benzene		Tetrahydro-3,5- dimethyl-2H-1,3,5-thiadiazine-2-thione (a.k.a. Dazomet)	NHP
Ethylene glycol		Tetrasodium ethylenediamine tetraacetate	
Ethylene oxide		Thioglycolic acid	
Formaldehyde	NHP	Thiourea	
Glutaraldehyde		Toluene	HS
Hydrochloric acid		Trisodium nitrilotriacetate	
Hydrogen peroxide		Xylene	HS

*Note see Table A2

A more-comprehensive list is provided in an updated report (New York State, 2011), which is too long to reproduce.

Table A2 Measured flowback water composition (reproduced in Woods et al. 2010)

Parameter	No of samples	No of detects	Min	Median	Max	Controlled substance*
1,4-dichlorobutane (%REC)	1	1		198		
2,4,6-tribromophenol (%REC)	1	1		101		
2,4-fluorobiphenyl (%REC)	1	1		71		
2-fluorophenol (%REC)	1	1		72.3		
4-nitroquinolone-1-oxide (mg/L)	24	24	1422	13908	48336	
4-terphenyl-d14 (%REC)	1	1		44.8		
Acetone (µg/L)	3	1		681		
Alkalinity (mg/L)	31	9	4.9	91	117	
Aluminium (mg/L)	29	3	0.08	0.09	1.2	
Antimony (mg/L)	29	1		0.26		
Aqueous ammonia (mg/L)	28	25	12.4	58.1	382	NHP
Arsenic (mg/L)	29	2	0.09	0.107	0.123	
Barium (mg/L)	34	34	0.553	661.5	15700	
Benzene (µg/L)	29	14	15.7	479.5	1950	HS/PS
BOD (mg/L)	29	28	3	274.5	4450	
Bis(2-ethylhexyl)phthalate (µg/L)	23	2	10.3	15.9	21.5	PS
Boron (mg/L)	26	2	0.539	2.06	26.8	
Bromide (mg/L)	6	9	11.3	616	3070	
Bromoform (µg/L)	29	6	34.8	36.7	38.5	
Cadmium (mg/L)	29	5	0.009	0.032	1.2	HS/PHS
Calcium (mg/L)	55	52	29.9	5198	34000	
COD (mg/L)	29	29	1480	5500	31900	
Chloride (mg/L)	58	58	287	56900	228000	
Chlorodibromomethane (µg/L)	29	2	3.28	3.67	4.06	
Chromium (mg/L)	29	3	0.122	5	5.9	
Cobalt (mg/L)	25	4	0.03	0.40	0.58	NHP
Copper (mg/L)	29	4	0.01	0.035	0.157	
Cyanide (mg/L)	7	2	0.006	0.013	0.019	
Dichlorobromomethane (µg/L)	29	1		2.24		
Ethyl benzene (µg/L)	29	14	3.3	53.6	164	
Fluoride (mg/L)	4	2	5.23	393	780	
Iron (mg/L)	58	34	0	47.9	810	
Lead (mg/L)	29	2	0.02	0.24	0.46	PS
Lithium (mg/L)	25	4	34.4	55.8	161	
Magnesium (mg/L)	58	46	9	563	3190	
Manganese (mg/L)	29	15	0.0292	2.18	14.5	
Methyl bromide (µg/L)	29	1		2.04		
Methyl chloride (µg/L)	29	1		15.6		
Molybdenum (mg/L)	25	3	0.16	0.72	1.08	
Naphthalene (µg/L)	26	1		11.3		HS/PS

Parameter	No of samples	No of detects	Min	Median	Max	Controlled substance*
Nickel (mg/L)	29	6	0.01	0.047	0.137	PS
Nitrogen (total as N) (mg/L)	1	1		13.4		
Oil and grease (mg/L)	25	9	5	17	1470	HS
o-terphenyl	1	1		91.9		
pH	56	56	1	6.2	8.0	
Phenol (µg/L)	23	1		459		NHS
Phenols (µg/L)	25	5	0.05	0.191	0.44	NHS
Phosphorus (as P) (mg/L)	3	3	0.89	1.85	4.46	
Potassium (mg/L)	31	13	59	206	7810	
Selenium (mg/L)	29	1		0.058		
Silver (mg/L)	29	3	0.129	0.204	6.3	
Sodium (mg/L)	31	28	83.1	19650	96700	
Strontium (mg/L)	30	27	0.501	821	5841	
Sulphate (as SO ₄) (mg/L)	58	45	0	3	1270	
Sulphide (as S) (mg/L)	3	1		29.5		
Sulphite (as SO ₃) (mg/L)	3	3	2.56	64	64	
Surfactants (mg/L)	3	3	0.2	0.22	0.61	
Tetrachloroethene (µg/L)	29	1		5.01		HS/Other
Thallium (mg/L)	29	1		0.1		
Titanium (mg/L)	25	1		0.06		
Toluene (µg/L)	29	15	2.3	833	3190	HS
Total dissolved solids (mg/L)	58	58	1530	93200	337000	
Total Kjeldahl nitrogen (mg/L)	25	25	37.5	122	585	
Total organic carbon (mg/L)	23	23	69.2	449	1080	
Total suspended solids (mg/L)	29	29	30.6	146	1910	
Xylenes (µg/L)	22	14	16	487	2670	HS
Zinc (mg/L)	29	6	0.028	0.048	0.09	
Gross alpha (pCi/L)	8	8	22.4		18950	
Gross beta (pCi/L)	8	8	62		7445	
Total alpha radium (pCi/L)	6	6	3.8		1810	
Radium-226 (pCi/L)	3	3	2.58		33	
Radium-228 (pCi/L)	3	3	1.15		18.41	

***Note**

Groundwater (under GWDD)(JAGDAG, 2011)

Hazardous substance (HS)

Non-hazardous pollutant (NHP)

Surface water (under Priority Substances Directive)(EC, 2008)

Priority Hazardous Substance (PHS)

Priority Substance (PS)