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Review of groundwater monitoring data, KM8 Site, Kirby Misperton

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1. INTRODUCTION

In April 2016, the Environment Agency granted Third Energy an Environmental Permit for activities that relate to the exploration for and extraction of natural gas from an existing well (KM8) by hydraulic fracturing, at their Kirby Misperton A (KMA) well site.

Hydrocarbon activities have been undertaken at the site by Third Energy and its predecessor for many years, including the disposal of waste produced water into the Kirkham Abbey Formation at borehole KM3.

A condition of the 2016 permit is that

At least 4 weeks prior to commencement of permitted activities, the operator shall submit to the Environment Agency for prior approval an updated Emissions Monitoring Plan (EMP) which shall include but is not limited to...

...Complete details of the baseline surface water and groundwater study undertaken prior to activities commencing; and details of any changes made to the groundwater and surface water monitoring programme proposed. Baseline monitoring shall include as a minimum the parameters listed in Table S3.5; and the locations, depth, construction method of the monitoring boreholes

The EMP and a baseline monitoring report have been issued and are publicly available on the Environment Agency website.

Friends of the Earth (FoE) has commissioned H Fraser Consulting (HFCL) to review the baseline monitoring report.

1.1 Objective

The objectives of the review are to address the following questions:

Adequacy of the monitoring data set

Has the monitoring been carried out properly and in accordance with relevant standards?

Is the monitoring based on a credible hydrogeological model (and is that model supported by the results?)

Was the EA right to allow Third Energy not to monitor certain elements?

Data interpretation

Are the levels of methane in the Corallian aquifer high? Are they harmful (e.g. to humans or animals)? Are they contrary to relevant standards?

What has caused the high levels? In particular, can we link them to Third Energy's disposal of large quantities of produced waste over many years at KM3?

Has Third Energy overlooked elevated levels of other pollutants besides methane?

Conclusion

Can the minister robustly grant hydraulic fracking consent given the levels of pollutants in the groundwater, the risk that fracking could compound these, potential problems with monitoring and any uncertainty which remains?

1.2 Scope of works

The following works have been undertaken:

- Review of the following documents
 - Document 1 KMA Report rev6_full2_Redacted
 - Document 2 KMA Baseline Water Quality Data Appendix E - Analysis Results R1
 - Document 3 KMA Baseline Water Quality Data_April to June 2017_Redacted
 - Document 4 KMA Baseline Water Quality App D - Analysis Results 2017
 - Document 5 Additional information on groundwater monitoring parameters
 - Document 6 Technical note on groundwater monitoring parameters (SoM Tech Note)
 - Document 7 Briefing note on groundwater monitoring scheme
 - Document 8 Review of scientific literature relating to methane in groundwater
- Reporting

2 ASSESSMENT

The baseline monitoring dataset comprises 21 monitoring rounds from February 2015 to September 2016 (Doc. 1). A further three monitoring rounds from April, May and June 2017 (monitoring rounds 23 – 25, Doc. 3) are also reported separately. Monitoring round 22 is not reported. Sampling has been undertaken at four surface water locations, six off-site groundwater locations and five boreholes drilled for the purpose at the KMA well site. The five purpose drilled boreholes were included in the sampling programme from monitoring round 15 onwards.

Has the monitoring been carried out properly and in accordance with relevant standards?

The KMA report makes reference to the following sampling protocol:

Groundwater and Surface water Sampling Protocol, Prepared by Envireau Water for Third Energy UK Gas Ltd, October 2016.

This document has not been reviewed, however it is noted that the Sampling Protocol report is dated October 2016, after the first 21 monitoring events were complete. Section 1.3 of the baseline monitoring report (Doc. 1) states that groundwater monitoring was undertaken by Third Energy. It is not clear therefore, whether the sampling was undertaken by Envireau Water according to pre-existing and established sampling protocols, or whether Third Energy undertook sampling and the Sampling Protocol described the methodology 'after the event'.

Samples from the first 14 monitoring rounds were submitted to ESG laboratories for analysis of a limited suite of chemicals that did not reflect the requirements of the Environmental Permit for two reasons:

1. The following determinands were not analysed:
 - Methane, carbon dioxide, acrylamide, arsenic, antimony, barium, beryllium, BOD, boron, bromide, $\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-CO}_2$, cadmium, carbon dioxide, chromium, cobalt, COD, copper, lead lithium, mercury, nickel, ORP, pH, salinity, selenium, silver, strontium, benzene, toluene, ethylbenzene, xylene, MTBE, TSS, vanadium, zinc, acetic acid, sodium persulphate, formaldehyde, ethylene glycol, phosphate.
2. The five boreholes BHA – BHE were not included in the monitoring

In addition, key analytical methods were not accredited, including for dissolved methane.

Samples from monitoring rounds 15 – 21 and 23 – 25 were submitted to Jones Laboratory; 11 of the 22 test methods used in the analysis are UKAS accredited.

Samples from monitoring rounds 16 – 18 were not analysed for methane gas, carbon dioxide, boron, bromide, or non-ionic surfactants. In addition, only a selection of the samples were analysed for the remainder of the full analytical suite specified in the environmental permit (as modified by Doc. 6). Many samples were not analysed for acrylamide, alkalinity, ammoniacal nitrogen, arsenic, antimony, barium, beryllium, BOD, boron, bromide, cadmium, chromium, cobalt, COD, copper, dissolved butane, dissolve propane, dissolved ethane, dissolved methane, fluoride, lead, lithium, mercury, nickel, nitrate, nitrite, salinity, selenium, silver, strontium, TDS, TSS, vanadium, zinc, phosphate, acetic acid, anionic surfactants, formaldehyde and ethylene glycol.

Samples from monitoring rounds 19 to 21 were analysed for a restricted suite which did not include methane gas, carbon dioxide, acrylamide, ammoniacal nitrogen, arsenic, antimony, barium, beryllium, BOD, boron, bromide, cadmium, calcium, chromium, cobalt, COD, copper, dissolved butane, dissolved propane, dissolved ethane, fluoride, lead, lithium, mercury, nickel, nitrate, nitrite, salinity, selenium, silver, strontium, TSS, vanadium, zinc, phosphate, acetic acid, anionic surfactants, non-ionic surfactants, formaldehyde, or ethylene glycol.

Samples from monitoring rounds 23, 24 and 25 were analysed for the full suite of parameters outlined in Doc. 6. $\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-CO}_2$ were analysed in monitoring rounds 15, 16, 17, 18, 21, 23, 24 and 25.

There are therefore only three monitoring rounds which meet the requirements of the Environmental permit, as amended by Doc. 6, from April, May and June 2017. This is considered an insufficient baseline against which to compare future monitoring data, as it does not include a full range of seasonal variation. British Standard BS10175 states that:

Groundwater levels vary during the year in response to a variety of factors, including changing weather conditions and plant transpiration rates. Obtaining a full picture of annual variations requires monitoring over 12 months, and could require several years.'

The period of monitoring from April to June 2017 is considered too short to properly characterise the baseline conditions in and around the KMA wellsite. The monitoring period does not capture the highest stream flows and groundwater levels in the winter or the lowest stream flows and groundwater levels in the summer.

An ion balance can be used to check analytical results. Total anions must be in balance with total cations, and the ratio of total anions to total cations should be 1. A greater imbalance indicates either inaccuracy in the analytical results or the presence of additional ions (potentially associated with organic material) that have not been taken into consideration in the analysis. An ionic balance within +/- 10% is generally considered acceptable.

An ionic balance has been carried out on the sample results from BHE in March 2016, and the results give a charge imbalance of 24%. This places significant doubt over the validity of the sample results, as it suggests that either there is a significant error in one or more of the analytical results, or that there is a major component of the groundwater chemistry that has not been analysed for.

Ion balances will have very likely been calculated by Envireau Water consultants as part of developing the Piper Diagrams presented in their reports. The results of these ion balances should be requested along with an explanation of any significant imbalances. Particularly, if there is uncertainty in the analytical results, this should be quantified so that the likely range of variation in baseline chemistry is properly defined.

Methane monitoring

Section 4A of the Petroleum Act 1998 is clear that 12 months' monitoring of methane in groundwater before fracking starts must be carried out.

Methane gas was monitored in the headspace of boreholes BHA, BHB, BHC, BHD and BHE and in air at surface water sampling locations and G1 – G6 on three occasions (April, May and June 2017).

Dissolved methane has been measured in water samples as follows:

- | | |
|--------------------|--|
| G1, G2, G3 and G5: | 22 or 23 samples over 2 years and 2 months. 22 or 23 samples approximately monthly from Feb/Mar 2015 to September 2016. 3 further samples in April, May and June 2017. |
| G4: | 9 samples over 2 years and 2 months. 6 samples from March April May July Aug and September 2016, 3 further samples in April, May and June 2017. |

- G6: 6 samples over 1 year and 10 months. 3 samples in July, August and September 2016, 3 further samples in April, May and June 2017.
- BHA, BHB, BHC, BHD, BHE: 10 samples over 1 year and 13 months. 7 samples from March to September 2016, 3 samples from April May and June 2017.

There is therefore not a complete record of 12 months monitoring of dissolved methane in groundwater across the monitoring network.

Gas monitoring

Methane monitoring was undertaken during monitoring rounds 23, 24, and 25, as background monitoring at surface water sites and as borehole headspace monitoring at boreholes. Soil gas flows and concentrations are heavily influenced by atmospheric pressure and ambient conditions such as temperature and the saturation state of the ground. It is important to obtain measurements when atmospheric pressure is low and falling¹. The monitoring records do not detail ambient conditions. Background gas concentrations could be significantly different under summer or winter conditions, and it is considered that the monitoring period is too short to reflect the full range of possible gas concentrations and flows.

Is the monitoring based on a credible hydrogeological model (and is that model supported by the results?)

The underlying geological sequence is of Drift Deposits, overlying Kimmeridge Clay, overlying the Corallian Limestone. The target strata for fracking is the Carboniferous Bowland Shale Formation, at a depth of c. 2000 – 3100 m. The waste produced water injected at KM3 targets the Kirkham Abbey Formation, several hundred metres below the Corallian Limestone.

Further north in the area, the Corallian Limestone is unconfined, and is widely used for groundwater supply and forms a regionally important and sensitive water body. In the area of the KMA site, the Corallian Aquifer is confined below the Kimmeridge Clay and the groundwater quality is slightly brackish, with elevated chloride concentrations of 600- 700 mg/l, which make it unsuitable for drinking water supply. The aquifer is not widely used for groundwater supplies in the immediate area; borehole records and well records held by the BGS² indicate that wells sunk in the local area target the superficial deposits or the Kimmeridge Clay.

On the basis of the available information, the monitoring network seems reasonable, with the only caveat being that if the Corallian Limestone is locally impacted by produced water disposal at KM3, the borehole does not give a good indication of baseline chemistry.

Was the EA right to allow Third Energy not to monitor certain elements?

Envireau Water argue in their technical note (Doc. 6) that certain of the parameters specified in the Environmental Permit cannot be analysed in groundwater samples. This is supported by a letter to the Environment Agency (Doc. 7), detailing three reputable laboratories who confirmed that analysis of these compounds is not routinely available for groundwater samples.

The Environment Agency have issued a technical note which states that 'All chemicals that are to be used in the fracturing fluid have already been assessed as non-hazardous to groundwater.'

A review of the 7 compounds removed from the monitoring suggests that six of the compounds are unlikely to be harmful. Some doubt remains around Triacine (which refers to 1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol (T3T), found in Safe-Cide, a fracking additive). A brief review of the

¹ Wilson et al., 1997

² <http://mapapps2.bgs.ac.uk/geoindex/home.html>

literature indicates that TZT is not listed in the Environment Agency's Chemical Standards Database, and that it should readily biodegrade at concentrations of 50 mg/L or less should (Angus Chemical Co., 1997) The half life of TZT is 5.67 days.³

In conclusion, the suite of parameters agreed for the monitoring network seems reasonable.

2.1 Data interpretation

Are the levels of methane in the Corallian aquifer high? Are they harmful (e.g. to humans or animals)? Are they contrary to relevant standards?

Dissolved methane has been measured at concentrations ranging from 28.7 mg/l to 67 mg/l from BHE, in the Corallian Limestone.

The solubility limit of methane in water (at 25°C is 25 mg/l)⁴, and at this concentration, water would equilibrate with concentrations of methane gas in air above explosive thresholds⁵.

The fact that the concentrations are above the saturation limit indicate that the system is under pressure, giving rise to oversaturation. When brought to the surface, it would be expected that methane would degas, at potentially explosive concentrations in air.

Methane is non-toxic, but is an asphyxiant and forms explosive mixtures in air with oxygen. There are no standards for methane in drinking water in the UK, or Environmental Quality standards for methane in surface water or groundwater. The background quality of the Corallian aquifer is poor in this area, as it is confined by the Kimmeridge Clay and mineralised. It is not considered likely that the high methane concentrations in-situ present a risk to water resources, however if the groundwater were brought to surface there would be significant safety considerations regarding explosivity, flammability, and asphyxiation hazards. As the Corallian Limestone is confined by the Kimmeridge Clay, the only routes by which groundwater would reach the surface would be via a borehole.

What has caused the high levels? In particular, can we link them to Third's disposal of large quantities of produced waste over many years at KM3?

A brief review of methanogenesis

Methane in groundwater can be formed by thermogenic or biogenic means. The thermogenic process is by chemical 'cracking' of organic matter under high temperature and pressure – the process by which natural oil and gas is formed.

Biogenic methanogenesis is the creation of methane by the action of bacteria. Two primary types of methanogenesis are recognised; reduction of bicarbonate and fermentation of organic matter.

Three indicators have been examined to assess the possible origin of methane in the Corallian Limestone at BHE:

- Methane concentrations
- Redox chemistry
- Isotope ratios
- Presence of other hydrocarbons

³ <https://comptox.epa.gov/dashboard/dsstoxdb/results?search=1%2C3%2C5-Triazine-1%2C3%2C5%282H%2C4H%2C6H%29-triethanol>.

⁴ Wilson et. al (1997)

⁵ Edwards, 2012

Methane concentrations at BHE

Dissolved methane concentrations in the Corallian aquifer are significantly higher (28.7 mg/l to 67 mg/l) than those at other groundwater monitoring locations, and above the saturation limit. There is therefore a question as to whether these high concentrations could arise from in-situ methanogenesis, and whether similar concentrations have been observed elsewhere.

BGS dissolved methane data presented by Envireau Water exhibit concentrations of up to 50 mg/l in groundwater, although most samples are below 10 mg/l. The report states that these samples are from the Vale of Pickering, from the drift and/or Kimmeridge Clay Formation, but sample locations and depths are not known. The high results are observed to reduce over time. It is not known whether the methane observed is biogenic or thermogenic in origin.

Data from BGS samples in the Corallian Limestone are not presented by Envireau Water, as:

'the BGS data currently available from the Corallian Group in the Vale of Pickering is primarily from the unconfined Corallian on the margins of the Vale of Pickering. At this stage, it is therefore not possible to compare these data to the results from the Corallian borehole at the KMA Well site'

The BGS have been contacted to discover whether the same data could be made available for examination.

Darling and Goody (2006) undertook a review of methane in English groundwaters. They found that:

'Measurements of potable waters from Cretaceous, Jurassic and Triassic carbonate and sandstone aquifers reveal CH₄ concentrations of up to 0.5 mg/l but a mean value of <0.01mg/l. However, aquiclude and thermal waters from the Carboniferous and Triassic typically contain in excess of 1.5 mg/l. Such high concentrations have so far only been found at redox potentials below 0 mV.'

The highest methane concentration found in the Darling and Goody (2006) study was 16 mg/l.

Data from the BGS website show methane concentrations of up to 1.32 mg/l in the East Midlands area.⁶

Various web sources from the USA report methane in groundwater, but concentrations exceeding the saturation limit are often reported as >28 mg/l. Higher concentrations are often assumed to be thermogenic in origin.

There is some evidence, therefore that concentrations of the order of those observed at BHE have been observed elsewhere. The provenance of those concentrations (methanogenic or thermogenic) has not been evaluated.

Redox Chemistry

Reducing conditions (an oxygen reducing potential of <0 mV) are required for methanogenesis to occur, however the observed oxygen reducing potential in the groundwater samples from BHE ranges from +344 mV to +948 mV with an average of +948mV. The redox chemistry would indicate that methanogenesis was not operating at BHE, as redox conditions are positive.

The groundwater chemistry at BHE is anomalous for a number of reasons. Concentrations of calcium and magnesium are low, which is unusual for a carbonate aquifer. Sulphate concentrations are also very low; this might be the result of sulphate reducing bacteria; however these would only be active in reducing conditions (<0mRV), which are not observed in the redox

⁶ (<http://www.bgs.ac.uk/research/groundwater/shaleGas/methaneBaseline/resultsMidsAndYorks.html>)

potential data. This and the ion imbalance indicate the influence of unquantified factors on the groundwater chemistry at BHE.

Isotope ratios

Biogenic methanogenesis preferentially selects the lighter ^{12}C isotope, giving $\delta^{13}\text{C}_{\text{CH}_4}$ ratios that are more negative than standard, and more negative than thermogenic methane. Similarly, biogenically derived methane has a different $\delta\text{D}_{\text{CH}_4}$ signature than thermogenically derived methane. Whiticar (1999) provides a CD diagram for the classification of bacterial and thermogenic natural gas, which uses a combination of $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ information to assess the origin of methane.

For biogenic methane, $\delta^{13}\text{C}_{\text{CH}_4}$ typically ranges from -110‰ to -50‰, with methane generated by bacterial carbonate reduction generally having a $\delta^{13}\text{C}_{\text{CH}_4}$ less than -60‰, and methane generated by fermentation having a $\delta^{13}\text{C}_{\text{CH}_4}$ above -60‰. Thermogenic CH_4 generally has a $\delta^{13}\text{C}_{\text{CH}_4}$ range from roughly -50‰ to -20‰ (Whiticar, 1999). There is an overlap in the region $\delta^{13}\text{C}_{\text{CH}_4}$ -55‰ to -65‰, and ambiguities over methane origin can be resolved by plotting $\delta^{13}\text{C}_{\text{CH}_4}$ against $\delta\text{D}_{\text{CH}_4}$ results.

There are, however, many confounding factors such as the original isotopic concentration of the substrate (bicarbonate or organic matter), the extent to which the substrate has been depleted in ^{12}C , and mixing between methane of different sources.

The $\delta^{13}\text{C}$ ratios of -58.6‰ to -80.8‰ observed at BHE are nominally consistent with bacterial methanogenesis by reduction of bicarbonate, however the higher (less negative) values may equally be as a result of mixing with a thermogenic source. The lack of $\delta\text{D}_{\text{CH}_4}$ means that a conclusive origin cannot be inferred.

Presence of other hydrocarbons

Thermogenically derived methane may be associated with other hydrocarbon species. Examination of the monitoring data shows that dissolved ethane was detected at BHE at 9 ug/l in monitoring round 23 (April 2017), but no other hydrocarbons have been detected at BHE during the monitoring programme.

Has Third Energy overlooked elevated levels of other pollutants besides methane?

A brief review of the dataset indicates that metals typically associated with anthropogenic pollution (arsenic, barium, beryllium, boron, cadmium, chromium, copper, mercury, lead, nickel, selenium, vanadium, zinc) were generally not detected, or were detected at concentrations that do not give cause for concern.

Sodium persulphate was detected at BHA, BHB, BHC, BHD and BHE at concentrations up to 702 mg/l (BHB, May 2016). Concentrations are significant, and no explanation has been given in the monitoring report (Doc.1) for these concentrations. Sodium persulphate is a powerful oxidising agent and is used as a viscosity breaker in hydraulic fracturing fluids.⁷

Formaldehyde was also detected on one occasion (monitoring round 24, May 2017) at 1.3 mg/l at BHE. A total of 7 measurements have been made for formaldehyde. The former World Health Organisation drinking water standard for formaldehyde was 0.9 mg/l, and the UK non-statutory Environmental Quality Standard (EQS)⁸ is 0.05 mg/l. Formaldehyde could be naturally occurring,

⁷ <http://www.peroxychem.com/markets/oil-gas-production/hydraulic-fracturing-viscosity-breakers>

⁸ Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Dangerous Substances Directive) - List II substances

but it is also associated with petrochemical waste waters. On the basis of one measurement it is not possible to draw conclusions regarding the origin of the formaldehyde.

2.2 Conclusion

Can the minister robustly grant hydraulic fracking consent given the levels of pollutants in the groundwater, the risk that fracking could compound these, potential problems with monitoring and any uncertainty which remains?

The baseline monitoring does not comply with Section 4A of the Petroleum Act 1998, which requires that 'the level of methane in groundwater has, or will have, been monitored in the period of 12 months before the associated hydraulic fracturing begins.' There is not a continuous period of 12 months monitoring for methane across the network, and monitoring records extend only until June 2017.

24 rounds of monitoring data have been reported, at locations in and around the KMA wellsite, to provide a baseline data set in accordance with the conditions of the Environmental Permit. The first 21 sets of monitoring data are considered inadequate to fulfil the requirement of the Environmental Permit, on the basis that a substantial number of analytical parameters were not included. Additionally, the full monitoring network had not been installed for rounds 1 to 14.

There are three sets of monitoring data from April, May and June 2017 which include the parameters set out in Schedule 3.5.1 of the Environmental Permit, as modified by Document 6. Data for monitoring round 22 is not included in the reports reviewed. This monitoring period does not include the extreme temperatures, flow conditions and water level conditions of summer or winter, and cannot therefore provide a full baseline characterisation of the setting.

The results of ion balances for water samples should be provided, along with an explanation of any significant imbalances. Particularly, if there is uncertainty in the analytical results, this should be quantified so that the likely range of variation in baseline chemistry is properly defined.

Concentrations of methane are very high (from 28.7 mg/l to 67 mg/l) in the Corallian Limestone groundwater at BHE. There is considerable ambiguity over the origin of this methane; there is some evidence to indicate that it is naturally derived in-situ by methanogenesis, but the redox conditions at this location would not permit methanogenesis. If the methane is partially thermogenically derived, this may provide evidence that injection of produced water at KM3 has impacted groundwater quality in the Corallian Limestone, which would in turn indicate a lack of integrity in the borehole seals/casing at KM3. This is relevant to the conditions of the Environmental Permit in so far as, if BHE is impacted by existing operations, the dataset does not provide a true baseline of groundwater chemistry in the Corallian Limestone.

Further assessment of the chemistry at BHE is required to explain the high concentrations of methane. Greater confidence in the baseline data could be achieved by

- A robust explanation of the major ion and redox chemistry at BHE, along with more evidence of the provenance of methane, which could be supplied by δD_{CH_4} analysis
- Evidence of recent pressure testing at KM3 to demonstrate integrity of the borehole
- Additional baseline chemistry, including dissolved methane concentrations, from another borehole in the confined Corallian Limestone that is sufficiently far from KMA to rule out any influence of existing operation on groundwater quality.

In conclusion:

- The three complete monitoring rounds from the spring of 2017 do not provide a sufficient baseline dataset to characterise the surface water, groundwater and ground gas

chemistry arising from extreme winter and summer conditions; additional monitoring is required to provide a more comprehensive dataset covering the full range of seasonal variation, and including for gas monitoring at times of falling atmospheric pressure;

- a robust understanding of the baseline groundwater chemistry in the Corallian Limestone cannot be inferred from the data available, and further assessment is required to demonstrate that observed methane is naturally occurring, and that groundwater is not impacted by current operations; and
- Consent for hydraulic fracking should not be given until these matters are resolved.

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