# FracRisk

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| **Deliverable Number:** | 2.2 |
| **Work package number:** | 2 - Data Collection & Analysis |
| **Deliverable title** | Produced Water Geochemical Data |
| **Type** | Click here to enter text. |
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**Deliverable summary text:**

1. **Data Summary**

Unconventional hydrocarbons, such as coal bed methane and shale gas reserves, require extraction techniques that produce waste fluids. These fluids can be contaminated with oils and grease, salts, naturally occurring radionuclides, toxic heavy metals and organic compounds that require specialised treatment or disposal. Detailed characterisation and understanding of these fluids allows regulators and operators to choose the most effective, economic, and safe method of waste management available. In the UK where the industry is in it's infancy, operations have been limited to one instance of hydraulic fracturing for shale gas at Preese Hall in Lancashire, and one instance of coal bed methane extraction at Airth in Falkirk, hence data available to characterise and predict these fluids are limited. The Scottish Environmental Protection Agency sample produced water from operations in Airth and released one chemical analysis to the public, while The Environment Agency collected and analysed 7 samples from operations at Preese Hall, and Cuadrilla (the operators) collected and analysed 24. The mean, minimum and maximum values for comparable chemical constituents measured in produced waters from shale gas operations in Table 1, and for coal bed methane produced waters in Table 2.

Also displayed in these Tables (1 & 2) is a summary of the data available to chemically characterise water produced from shale gas and coal bed methane operations across the USA. Figure 1 displays the spatial distribution of samples collected for the USA dataset.

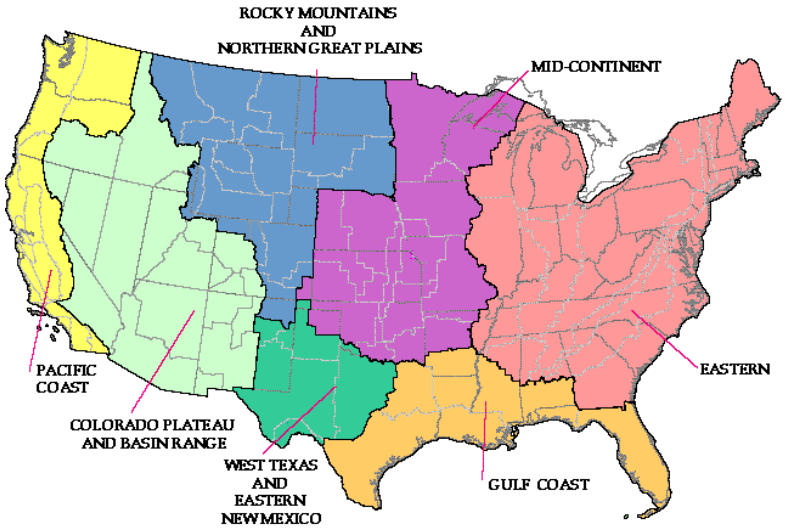


Figure 1 - Map of the USGS Regions based on National Assessment of US Oil and Gas Resources (1995)

- *CBM Rocky Mountains and Northern Great Plains (n=2992)*
- *CBM Mid Continent (n=2)*
- *CBM Eastern (n=126)*
- *CBM Colorado Plateau and Basin Range (n = 666)*
- *SG Rocky Mountains and Northern Great Plains (n=53)*
- *SG Mid Continent (n=2531)*
- *SG Eastern (n=508)*

Table 1 – Mean, minimum and maximum concentrations of comparable constituents in the flowback and produced waters from shale gas operations in the USA and UK.

| **Produced and Flowback Waters Composition** | **Shale Gas, UK** (n=31) | | | **Shale Gas, USA** (n=) | | |
|---|---|---|---|---|---|---|
| | ***Minimum (mg/l)*** | ***Mean (mg/l)*** | ***Maximum (mg/l)*** | ***Minimum (mg/l)*** | ***Mean (mg/l)*** | ***Maximum (mg/l)*** |
| ***pH*** | 5.40 | 5.78 | 6.10 | 3.20 | 7.55 | 11.80 |
| ***Alkalinity as HCO3*** | 41.00 | 81.21 | 133.00 | 76.90 | 190.63 | 440.00 |
| ***TSS*** | 230.00 | 1,387.00 | 2,600.00 | 4.00 | 316.00 | 5,290.00 |
| ***TDS*** | 94,000.00 | 168,750.00 | 210,000.00 | 221.00 | 88,198.00 | 345,000.00 |
| ***COD*** | 120.00 | 1,302.00 | 3,240.00 | 10.00 | 5863.07 | 51,000.00 |
| ***Silver*** | 0.00 | <1.00 | 0.00 | 0.00 | 0.04 | 0.10 |
| ***Arsenic*** | 0.48 | 0.97 | 1.40 | 0.01 | 0.07 | 0.15 |
| ***Barium*** | 9.20 | 19.03 | 30.00 | 0.06 | 1,076.40 | 13,600.00 |
| ***Vanadium*** | 0.00 | <5.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| ***Cobalt*** | 0.02 | 0.04 | 0.05 | 0.00 | 1.43 | 25.00 |
| ***Chromium*** | 0.00 | 0.05 | 0.30 | 0.00 | 1.80 | 155.50 |
| ***Manganese*** | 1.60 | 2.09 | 2.80 | 0.01 | 4.04 | 24.00 |
| ***Iron*** | 4.20 | 13.42 | 23.00 | 0.18 | 58.26 | 220.00 |
| ***Mercury*** | 0.00 | <0.20 | 0.00 | 0.00 | 0.00 | 0.00 |
| ***Nickel*** | 0.16 | 0.32 | 0.88 | 0.00 | 0.94 | 19.20 |
| ***Copper*** | 0.08 | 0.13 | 0.30 | 0.01 | 0.25 | 1.57 |
| ***Zinc*** | 0.00 | <0.50 | 0.00 | 0.04 | 2.00 | 182.00 |
| ***Cadmium*** | 0.12 | 0.12 | 0.12 | 0.00 | 0.03 | 0.10 |
| ***Lead*** | 0.03 | 0.05 | 0.05 | 0.00 | 0.05 | 0.65 |
| ***Fluoride*** | 0.00 | <50.00 | 0.00 | 0.01 | 3.06 | 58.30 |
| ***Chloride*** | 48,000.00 | 84541.00 | 100,000.00 | 18.00 | 51,714.70 | 196,000.00 |
| ***Sulphate*** | 579.00 | 570.00 | 570.00 | 0.78 | 58.84 | 374.00 |
| ***Nitrate*** | 0.00 | <100.00 | 0.00 | 0.02 | 2.17 | 15.9 |

Table 2 – Mean, minimum and maximum concentrations of comparable constituents in the flowback and produced waters from coal bed methane operations in the USA and UK.

| Produced and Flowback Waters from Coal Bed Methane Operations | CBM UK (n=1) | | | CBM USA, (n=3787) | | |
|---|---|---|---|---|---|---|
| | *Minimum (mg/l)* | *Mean (mg/l)* | *Maximum (mg/l)* | *Minimum (mg/l)* | *Mean (mg/l)* | *Maximum (mg/l)* |
| ***pH*** | - | 6.89 | - | 0.10 | 8.02 | 10.42 |
| ***Alkalinity as CaCO3*** | - | 416.00 | - | 770.00 | 1,506.87 | 3,300.00 |
| ***TSS*** | - | 60.20 | - | 1.00 | 32.18 | 580.00 |
| ***Chloride*** | - | 12,300.00 | - | 0.81 | 344.22 | 110,000.00 |
| ***Copper*** | - | 0.02 | - | 0.00 | 0.09 | 4.60 |
| ***Lead*** | - | 0.01 | - | 0.00 | 0.39 | 8.89 |
| ***Nickel*** | - | 0.04 | - | 0.00 | 0.05 | 2.61 |
| ***Zinc*** | - | 0.02 | - | 0.00 | 0.68 | 51.00 |
| ***Aluminium*** | - | 0.01 | - | 0.01 | 0.19 | 2.90 |
| ***Iron*** | - | 68.50 | - | 0.00 | 11.61 | 4,180.00 |
| ***Manganese*** | - | 0.79 | - | 0.00 | 0.13 | 6.00 |
| ***Mercury*** | - | 0.01 | - | 0.00 | 0.01 | 0.05 |
| ***Sulphate*** | - | 0.24 | - | 0.01 | 73.32 | 1,800.00 |

For shale gas operations, it can be useful to characterise the produced and flowback water compositions according to the shale they have been produced from. It is thought that some chemical variations can be explained due to changes in shale geochemistry. Due to the limited data available for the UK (one fracturing event, of one shale basin), this comparison is only possible for the US dataset. Tables 3, 4, and 5 display the minimum, mean and maximum values measured for each chemical constituent by shale basin. They also display the number of measurements (N) and the standard deviation (St. Dev.) from the calculated mean.

Table 3: Marcellus (n=247)
Table 4: Antrim (n=244)
Table 5: Woodford (n=2510)

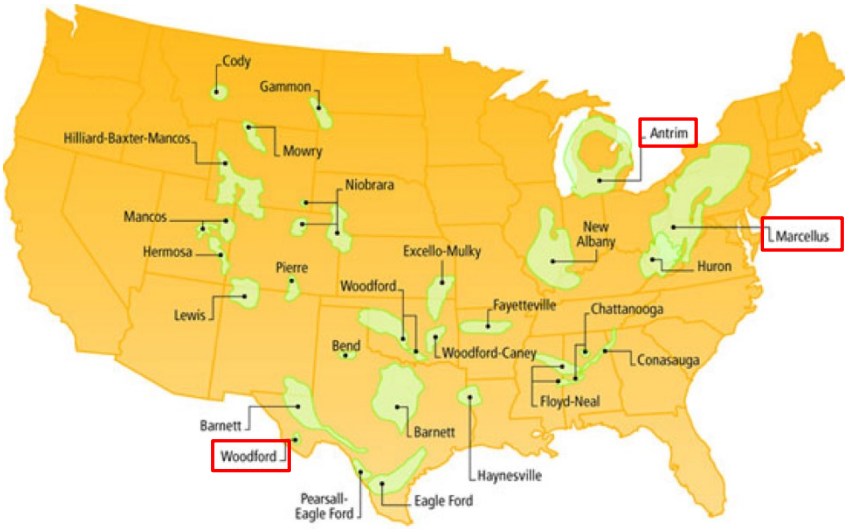


Figure 2 - Map of the US Shale Gas Basins, US Department of Energy (Baker Hughes, http://public.bakerhughes.com/shalegas/fracturing.html, 2011)

Table 3

Marcellus Shale Produced Waters

| Statistic | N | Mean | St. Dev. | Min | Max |
|---|---|---|---|---|---|
| PH | 104 | 6.699 | 0.864 | 4.900 | 11.800 |
| TDS | 106 | 88,196.680 | 89,003.680 | 221 | 345,000 |
| TSS | 97 | 316.134 | 653.441 | 4.000 | 5,290.000 |
| Ag | 85 | 0.044 | 0.020 | 0.002 | 0.100 |
| Al | 89 | 0.672 | 0.692 | 0.040 | 2.000 |
| As | 87 | 0.075 | 0.036 | 0.009 | 0.151 |
| B | 135 | 15.967 | 20.220 | 0.014 | 155.000 |
| Ba | 110 | 1,076.405 | 2,117.984 | 0.057 | 13,600.000 |
| Be | 85 | 0.036 | 0.016 | 0.0003 | 0.080 |
| Br | 145 | 542.183 | 430.553 | 0.200 | 1,990.000 |
| Ca | 129 | 7,023.768 | 7,684.812 | 5.450 | 41,000.000 |
| Cd | 88 | 0.031 | 0.023 | 0.001 | 0.100 |
| Cl | 103 | 51,714.700 | 53,011.780 | 18.000 | 196,000.000 |
| Co | 100 | 1.425 | 2.890 | 0.001 | 25.000 |
| Cr | 88 | 1.802 | 16.573 | 0.001 | 155.504 |
| Cs | 21 | 0.246 | 0.083 | 0.067 | 0.358 |
| Cu | 108 | 0.247 | 0.239 | 0.010 | 1.570 |
| F | 85 | 3.062 | 7.303 | 0.009 | 58.300 |
| Fe | 159 | 58.258 | 58.593 | 0.175 | 220.000 |
| Hg | 87 | 0.0002 | 0.0002 | 0.00002 | 0.001 |
| I | 5 | 25.700 | 4.018 | 19.900 | 29.900 |
| K | 145 | 396.487 | 598.540 | 2.590 | 4,080.000 |
| Li | 148 | 75.046 | 75.920 | 0.009 | 426.000 |
| Mg | 130 | 661.557 | 675.218 | 1.090 | 3,427.005 |
| Mn | 151 | 4.038 | 4.330 | 0.012 | 24.000 |
| Mo | 87 | 0.222 | 0.202 | 0.004 | 0.800 |
| NO2 | 84 | 10.441 | 21.535 | 0.034 | 146.000 |
| NO3 | 86 | 2.170 | 2.141 | 0.020 | 15.900 |
| NH4 | 98 | 97.912 | 100.146 | 0.280 | 441.000 |
| Na | 100 | 26,527.840 | 46,707.610 | 27.400 | 434,403.000 |
| Ni | 100 | 0.934 | 2.757 | 0.001 | 19.200 |
| Pb | 91 | 0.052 | 0.082 | 0.001 | 0.647 |
| Rb | 21 | 0.765 | 0.174 | 0.382 | 0.965 |
| S | 87 | 3.071 | 1.187 | 0.800 | 8.800 |
| Sb | 85 | 0.073 | 0.048 | 0.003 | 0.200 |
| Se | 85 | 0.046 | 0.018 | 0.003 | 0.100 |
| Sn | 85 | 0.851 | 0.450 | 0.004 | 2.000 |
| Sr | 165 | 1,449.971 | 1,560.729 | 0.074 | 8,460.000 |
| Ti | 85 | 0.268 | 0.198 | 0.010 | 0.500 |
| Tl | 86 | 0.141 | 0.166 | 0.004 | 1.000 |
| Zn | 110 | 2.004 | 17.325 | 0.036 | 182.000 |
| Alkalinity (CaCO3) | 102 | 139.560 | 116.152 | 5.000 | 592.000 |
| Alkalinity (HCO3) | 21 | 173.271 | 61.641 | 76.900 | 364.000 |
| DOC | 86 | 316.985 | 688.997 | 3.300 | 5,960.000 |
| TOC | 86 | 297.400 | 661.389 | 1.200 | 5,680.000 |
| BOD | 100 | 493.927 | 1,304.478 | 2.000 | 12,400.000 |
| COD | 100 | 6,117.403 | 7,898.401 | 35.300 | 47,400.000 |
| ALPHA | 31 | 12,501.670 | 22,595.260 | 14.100 | 123,000.000 |
| BETA | 30 | 2,053.038 | 2,725.899 | 6.790 | 12,000.000 |
| dD | 63 | -39.984 | 3.692 | -49.100 | -30.200 |
| $d^{13}C$ | 4 | 4.575 | 2.910 | 1.200 | 8.200 |
| $d^{18}O$ | 63 | -2.169 | 0.988 | -5.900 | -0.400 |
| $Sr^{87}/Sr^{86}$ | 61 | 0.711 | 0.0002 | 0.710 | 0.712 |
| $Ra^{226}$ | 31 | 3,975.955 | 5,400.795 | 0.163 | 16,920.000 |
| $Ra^{228}$ | 31 | 425.095 | 444.462 | 0.029 | 1,287.000 |

Table 4

Antrim Shale Produced Waters

| Statistic | N | Mean | St. Dev. | Min | Max |
|---|---|---|---|---|---|
| pH | 225 | 6.670 | 0.628 | 4.800 | 8.400 |
| TDS | 107 | 112,477.800 | 72,790.370 | 348 | 260,464 |
| B | 51 | 5.527 | 1.227 | 2.110 | 8.310 |
| Ba | 62 | 66.428 | 54.403 | 0.120 | 253.000 |
| Br | 192 | 170.737 | 129.527 | 1.598 | 639.272 |
| $HCO^3$ | 42 | 179.207 | 866.597 | 0.010 | 5,500.000 |
| Ca | 200 | 46,646.620 | 48,897.960 | 14.000 | 162,324.000 |
| Cl | 107 | 72,185.020 | 49,066.930 | 70.906 | 188,007.300 |
| Cs | 1 | 0.088 | | 0.088 | 0.088 |
| Fe | 59 | 83.749 | 67.832 | 0.290 | 251.000 |
| I | 1 | 2.000 | | 2 | 2 |
| K | 69 | 381.339 | 195.834 | 3.500 | 732.000 |
| Li | 53 | 12.801 | 6.772 | 1.990 | 27.300 |
| Mg | 66 | 2,503.387 | 1,493.777 | 4.400 | 5,560.000 |
| Mn | 51 | 0.977 | 0.894 | 0.100 | 6.480 |
| Na | 241 | 37,417.940 | 24,971.610 | 229.898 | 93,108.690 |
| SO3 | 1 | 1.800 | | 1.800 | 1.800 |
| SO4 | 39 | 40.686 | 103.563 | 0.100 | 641.770 |
| Si | 51 | 6.022 | 1.695 | 2.850 | 8.680 |
| Sr | 60 | 257.841 | 129.894 | 17.700 | 598.000 |
| Alkalinity (CaCO3) | 61 | 1,139.207 | 462.219 | 81.900 | 2,345.716 |
| dD | 48 | -60.000 | 22.710 | -101.700 | -25.000 |
| $d^{18}O$ | 54 | -9.175 | 3.596 | -14.650 | -2.200 |
| $Sr^{87}/Sr^{86}$ | 1 | 0.710 | | 0.710 | 0.710 |

Table 5

Woodford Shale Produced Waters

| Statistic | N | Mean | St. Dev. | Min | Max |
|---|---|---|---|---|---|
| pH | 2,502 | 7.678 | 0.689 | 3.200 | 9.300 |
| TDS | 968 | 15,679.220 | 8,078.208 | 186 | 174,778 |
| Ba | 478 | 7.419 | 9.791 | 0.050 | 78.000 |
| CO2 | 915 | 307.124 | 209.411 | 0.198 | 2,247.000 |
| HCO3 | 2,481 | 1,190.751 | 408.755 | 11 | 13,880 |
| Ca | 2,486 | 130.562 | 193.767 | 8 | 7,984 |
| Cl | 2,482 | 7,304.216 | 3,628.500 | 1 | 43,000 |
| Fe | 996 | 23.945 | 21.292 | 1 | 217 |
| K | 33 | 196.312 | 478.294 | 5.700 | 2,800.000 |
| Mg | 987 | 30.051 | 47.462 | 5 | 632 |
| Na | 989 | 5,757.608 | 1,953.392 | 13.100 | 27,925.000 |
| SO4 | 2,403 | 200.827 | 165.948 | 1 | 3,580 |
| H2S | 875 | 2.176 | 2.138 | 0.200 | 25.000 |

**2. Data Limitations**

- Multiple data sources
- Inconsistency of data collection, e.g. sampling technique, analysis method, etc.
- Incomparable parameters across datasets

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