

Methane, Sr, and Ba in Maryland streams above the Marcellus Shale

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The Marcellus Shale, which has been a focus of natural gas exploitation employing horizontal drilling and hydraulic fracturing ('fracking') techniques, intersects the westernmost part of Maryland below Allegany and Garrett Counties. By temporarily suspending the licensing process, the governor of Maryland has created a unique window for monitoring the pre-fracking water quality baseline that was not available in many other states. We are using this opportunity to measure dissolved methane (CH₄), strontium (Sr), and barium (Ba) levels in water samples taken at 1–2-month intervals from 27 sites across 5 distinct catchments, each for a period of one year. Thermogenic CH₄ from the Marcellus Shale may enter surface or groundwater as a direct result of fracking, whereas Sr and Ba occur at high concentrations in produced water and may be released due to spills or well-casing failure.

Dissolved CH₄ concentrations were measured by GC and found to range spatially from below detection to ~0.5 μM and as high as 5.5 μM in some streams, consistent with data reported for pristine rivers elsewhere in the USA. Values are typically higher in late summer, suggesting that the CH₄ is biogenically produced *in situ*. We are presently attempting δ¹³C analysis of the dissolved CH₄ using cavity ring-down spectroscopy to confirm this. Preliminary results obtained via IRMS are inconclusive, but method development is ongoing.

Dissolved Sr and Ba concentrations were measured by ICP-MS and generally found to range spatially between 0.1 and 1.5 μM, with several streams displaying strong seasonal cycles. Molar Ba/Sr ratios are more constant in each stream, distributed around unity, with some showing Ba-enrichment and some Sr-enrichment. Dissolved concentrations of major ions (Na, K, Mg, Ca, Cl, SO₄, ANC) were also measured by ICP-AES, IC, and Gran titration. A ternary diagram of the cation data suggests that stream compositions are grouped in accordance with the complex geology of the Appalachian Plateau rather than catchment, perhaps explaining the spatial variability of Sr and Ba. Temporal variability may be driven by seasonal shifts in precipitation vs. groundwater inputs.

The observed significant variability of dissolved CH₄, Sr, and Ba levels in an area slated for natural gas exploitation may complicate recognition of potential future surface water contamination from fracking activities and emphasizes the need for longterm regional monitoring of pre-fracking water quality baselines with high spatial and temporal resolution.